











# JOURNAL

OF

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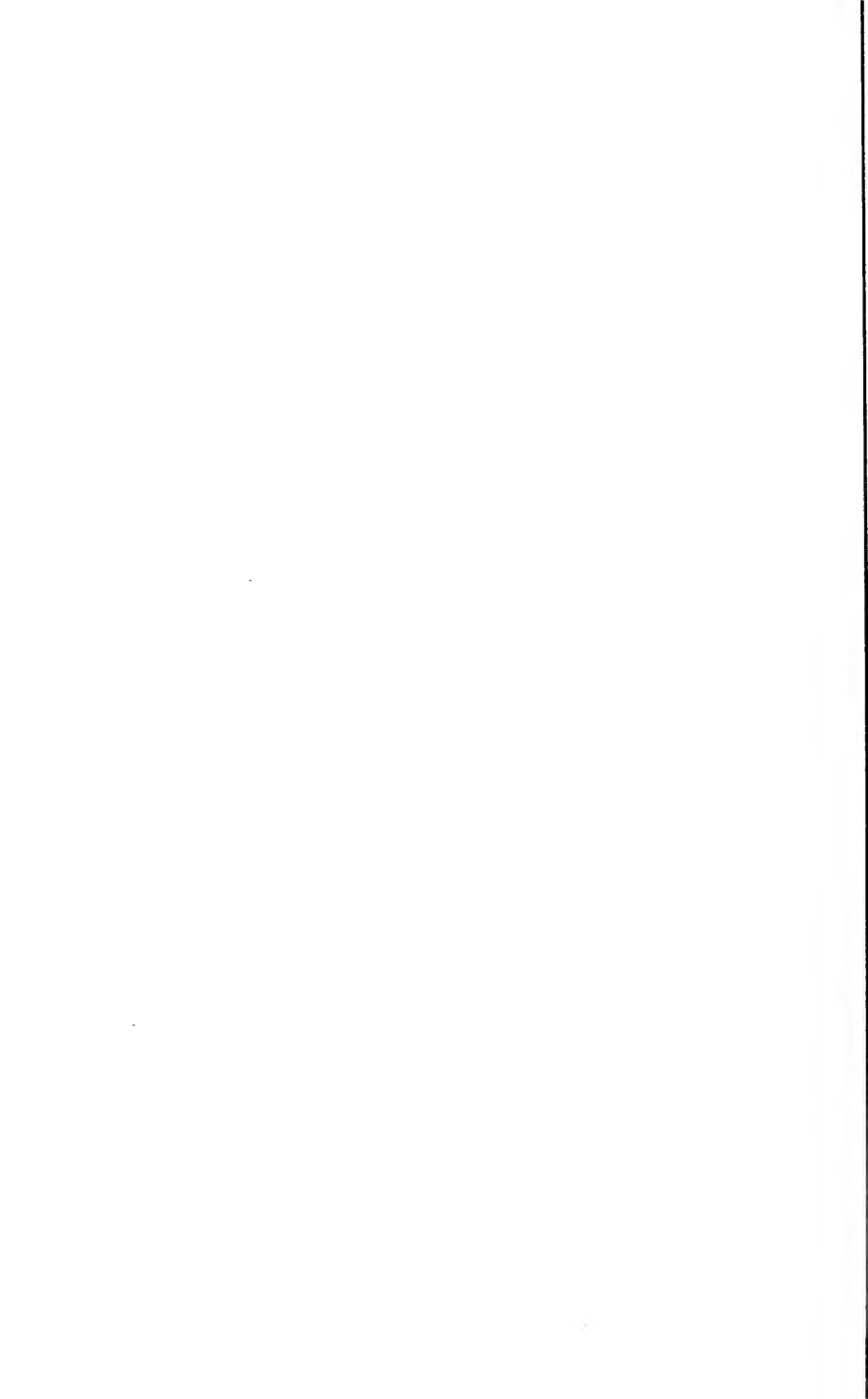


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PAPERS READ BEFORE THE CHEMICAL SOCIETY.

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### I.—*Some Derivatives of Pr 1*n*-Methylindole.*

By H. G. COLMAN, Ph.D., M.Sc.

#### *Introduction.*

IN his classic researches on the compounds of the indigo-group, Baeyer obtained, by the reduction of isatin, successively—

Dioxindole,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CH}(\text{OH}) \\ \text{—NH—}\end{smallmatrix}\rangle\text{CO}$ ; Oxindole,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CH}_2 \\ \text{NH}\end{smallmatrix}\rangle\text{CO}$ ;

and Indole,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CH} \\ \text{NH}\end{smallmatrix}\rangle\text{CH}$ .

Up to the present time, the methyl-derivatives of these compounds have been but little studied, and it seemed probable that they might be obtained from Pr 1*n*-methylindole (for nomenclature, see E. Fischer, *Annalen*, **236**, 116), which, thanks to the researches of E. Fischer and O. Hess (*Ber.*, **17**, 559), can now be prepared in quantity without difficulty.

Fischer and Hess (*ibid.*, p. 561) have shown that methylindole can be converted into methylpseudoisatin by a very remarkable reaction. They found that when methylindole or methylindolecarboxylic acid is treated with a solution of sodium hypochlorite, a crystalline precipitate is formed, which on boiling with alcoholic potash yields methylpseudoisatin.

The intermediate product was analysed by Fischer and Hess, but the analysis was insufficient to decide whether the substance had the formula  $\text{C}_9\text{H}_9\text{NBr}_2\text{O}$  or  $\text{C}_9\text{H}_7\text{NBr}_2\text{O}$ . At Professor Emil Fischer's

suggestion, I have made a detailed examination of the reaction, the results of which are given in the following paper.

The product of the action of sodium hypochlorite on methylindole or methylindolecarboxylic acid has the formula  $C_6H_7NBr_2O$ , and is most probably a dibromo-derivative of methyloxindole, having the formula  $C_6H_4<\overset{-CBr_2-}{N(CH_3)}>CO$ , since with phenylhydrazine it gives a crystalline derivative, which is identical with methylpseudoisatin-phenylhydrazone. The latter must have the constitution



as phenylhydrazine never reacts with a carbonyl-group which is directly combined with nitrogen (see Baeyer, *Ber.*, **16**, 2188). From this it follows that the two bromine-atoms must be in the Pr 3-position as given in the above formula.

This formula also easily explains the formation of methylpseudoisatin when the substance is boiled with alkali or even with water, the two bromine-atoms being displaced by one of oxygen.

By the action of sodium hypochlorite on methylindolecarboxylic acid, the corresponding dichloromethyloxindole is obtained, which corresponds in all its reactions to dibromomethyloxindole.

This peculiar reaction with hypochlorites and hypobromites seems confined to those indoles in which the alkyl-group is attached to the nitrogen-atom. If indole is treated in the corresponding manner, the products of the reaction are not nearly so simple.

Methylpseudoisatinoxime,  $C_6H_4<\overset{C(N\cdot OH)}{N(CH_3)}>CO$ , can be obtained in two ways, viz., by the action of hydroxylamine on methylpseudoisatin, or by passing nitrogen trioxide into a solution of methyloxindole.

On reduction in acid solution, dibromomethyloxindole loses first one atom of bromine, forming monobromomethyloxindole,



which by long-continued reduction loses the second atom of bromine, and is converted into methyloxindole,  $C_6H_4<\overset{-CH_2-}{N\cdot CH_3}>CO$ .

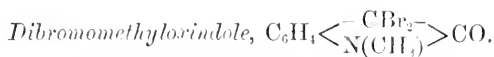
By the reduction of methylpseudoisatin in either acid or alkaline solution, methyldioxindole,  $C_6H_4<\overset{CH(OH)}{N(CH_3)}>CO$ , is obtained.

#### *Experimental Part.*

The methylindolecarboxylic acid necessary for this work was prepared according to the directions of Fischer and Hess (*Ber.*, **17**, 561),

by warming methylphenylhydrazone-pyroracemic acid with dilute hydrochloric acid. The crude acid thus obtained is sufficiently pure for further experiments.

The pyroracemic acid required was prepared by Döbner's method (*Annalen*, **242**, 268), which gives a very satisfactory yield of the pure acid.



The action of sodium hydrobromite on methylindolecarboxylic acid was found to proceed best under the following conditions:—

5 grams of the crude acid are dissolved in dilute caustic soda solution, and boiled with animal charcoal for a few minutes. The filtered liquid is gradually added to a well-cooled mixture of 22.5 grams of bromine in about 900 c.c. of water, to which sufficient caustic soda had been added to neutralise the bromine, and the whole continually shaken during the addition. The substance separates at once in fine needles, the colour of which, in the various experiments, varied from light brown to dark red.

In order to purify the substance, the crystals are collected, well washed with water, dissolved in alcohol and boiled with animal charcoal. The filtered solution is then partially evaporated, and on cooling small yellow tables crystallise out. These are separated from the mother-liquor on the filter-pump, twice recrystallised from alcohol, and finally dried over sulphuric acid in a vacuum.

By this means the substance is obtained in almost white tables, which melt with decomposition at 204°. On analysis, numbers were obtained,\* which agree well with the formula  $\text{C}_9\text{H}_7\text{NBr}_2\text{O}$ .

A comparison of this formula with that of methylindole shows that it differs from the latter in that it contains two atoms of hydrogen less, and the elements  $\text{Br}_2\text{O}$  more. As it is easily converted into methylpsendoisatin, the bromine substitution must have taken place in the pyrroline-ring. In order to determine whether these bromine-atoms are attached to the *same* or to *different* carbon-atoms, the substance was subjected to the action of phenylhydrazine.

For this purpose, 4 grams of the crude product were dissolved in warm alcohol, and added to a solution of 5 grams of phenylhydrazine hydrochloride, and 7.5 grams of sodium acetate dissolved in as little water as possible. In a short time, the liquid became dark brown, and on addition of water the product of the reaction was completely precipitated as a yellow oil, which crystallised on standing. The crystals were collected, washed, and twice recrystallised from benzene.

\* For analytical numbers, &c., in this and the remaining analyses, see *Annalen*, **248**, 114 &c.

It forms fascicular groups of small yellow needles which melt at 144—145° (uncorr.), and gave on analysis numbers agreeing with those required for methylpseudoisatin-phenylhydrazone. A comparison of its properties with the compound obtained from methylpseudoisatin and phenylhydrazine showed conclusively that the two substances were identical.

From this it follows that the two bromine-atoms are attached to the same carbon-atom in the pyrroline-ring, which condition is fulfilled only by the two following formulæ:—

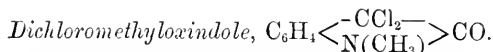


The first would be dibromomethyloxindole, and the second dibromomethylpseudoindoxyl.

The hydrazones of the compound under discussion and of methylpseudoisatin being identical, the two bromine-atoms in the one must correspond with that carbonyl-group in the other which is acted on by phenylhydrazine. Now, it is well known that phenylhydrazine never acts on a carbonyl-group which is directly connected with nitrogen, so that in methylpseudoisatin the carbonyl-group in the Pr 3-position must be the one attacked, and the hydrazone formed must have the formula  $\text{C}_6\text{H}_4 < \overset{\text{C}(\text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_5)}{\underset{\text{N}(\text{CH}_3)}{\text{—}}} > \text{CO}$ . It follows, therefore, that in the brominated compound the two bromine-atoms must also occupy the Pr 3-position, as given in the first of the above formulæ.

The substance consequently is dibromomethyloxindole. Its chief properties are as follows:—

It crystallises from alcohol in yellowish-white tables, which, when quickly heated, melt with decomposition at 204°. If heated slowly, however, it becomes brown at 170°, and melts at 180°. It is readily soluble in alcohol, ether, chloroform, and benzene, but only sparingly in light petroleum, and insoluble in cold water. On boiling with water, it is converted into methylpseudoisatin. It reacts very readily with alkalis, ammonia, amines, hydrazines, and reducing agents. If shaken with benzene containing thiophen and strong sulphuric acid, a brown coloration is produced, which, however, after standing for several hours, becomes changed to the same blue as that produced by methylpseudoisatin.

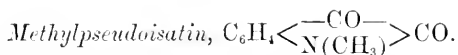


The preparation of this substance corresponds exactly with that of dibromomethyloxindole. The solution of methylindolecarboxylic acid in alkali is purified by boiling with animal charcoal, and



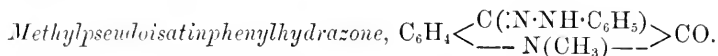
gradually added to a cold dilute solution of sodium hypochlorite, care being taken that the latter is in excess. The substance separates first in small oily drops, which soon solidify to small brownish-white needles. These are collected, well washed, and recrystallised several times from alcohol or acetone. Thus purified it forms white needles which melt at 145—147°. The numbers obtained on analysis agree well with those required by the formula  $C_9H_7NCl_2O$ .

Dichloromethyloxindole dissolves much more readily in alcohol than the corresponding bromine-compound, and is also easily soluble in acetone and ether, but insoluble in water. Towards reagents it behaves in exactly the same manner as dibromomethyloxindole, but it is not so easily decomposed by heat, for, whereas the former begins to decompose at 170°, the latter can be heated to 210° without any change taking place.



This compound was obtained by Fischer and Hess (*loc. cit.*) from dibromomethyloxindole by boiling it with alcoholic potash. Instead of this, it was found more advantageous to boil the bromine-compound with water. About 8 grams of crude dibromomethyloxindole are suspended in 300 grams water, and the whole boiled for two or three hours, using a reflux condenser. The solution becomes deep red, and a considerable quantity of resinous matter separates. This is filtered off, and the clear solution concentrated on the water-bath, when beautiful red needles separate on cooling; these, after another crystallisation from water, are quite pure.

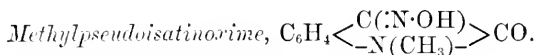
The properties of methylpseudoisatin have already been given by Fischer and Hess (*Ber.*, **17**, 561).



To prepare this substance, 1 gram of methylpseudoisatin is dissolved in hot water, and to this an aqueous solution of 1 gram of phenylhydrazine hydrochloride and 1.5 grams of sodium acetate is added. The solution becomes turbid almost immediately, and after a short time oily drops separate which crystallise on cooling. The crystals are collected, washed, recrystallised from alcohol or benzene, and dried at 100°. The results of its analysis are in full agreement with the above formula.

Methylpseudoisatinphenylhydrazone crystallises in fascicular groups of small, yellow needles, which melt without decomposition at 145—146°. It is easily soluble in alcohol and benzene, sparingly in ether, and insoluble in water and light petroleum.

As has already been stated, the product obtained by the action of phenylhydrazine on dibromomethyloxindole is identical with this hydrazone.



The preparation of this oxime is best carried out as follows:—

Aqueous solutions of methylpseudoisatin and hydroxylamine sulphate are mixed, and allowed to stand. The liquid soon becomes turbid, and in about 12 hours the reaction is complete, part of the oxime separating as a bulky amorphous precipitate, while part remains in solution.

In order to isolate the oxime, the whole is shaken with ether 10 times successively, the ethereal solution dried with calcium chloride, the ether distilled off, and the residue, which is a yellow, crystalline mass, purified by recrystallisation from hot water.

In this manner the oxime is obtained as a light yellow substance crystallising in small needles, which on heating become plastic at  $170^\circ$ , and melt at  $180\text{--}183^\circ$ . Even after repeated crystallisation from acetone, the melting point does not become constant. The corresponding ethylpseudoisatinoxime was found by Baeyer (*Ber.*, **16**, 2196) to behave in a similar manner.

Methylpseudoisatinoxime is fairly soluble in hot, but much less in cold water, easily in alcohol, acetone, ether, and benzene.

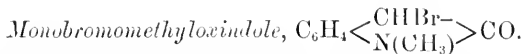
#### *Reduction of Dibromomethyloxindole in Acid Solution.*

Dibromomethyloxindole is very easily acted on by reducing agents, especially in acid solution. The reduction proceeds best as follows:—

To a mixture of dibromomethyloxindole with an excess of zinc-dust, suspended in alcohol, concentrated hydrochloric acid is gradually added in small portions, the whole being shaken after each addition. After a few minutes, the dibromomethyloxindole dissolves, forming a clear yellow solution, which is warmed for a short time on the water-bath. After the solution has been filtered from the unaltered zinc-dust, it is largely diluted with water, and heated on the water-bath till the alcohol is completely evaporated. The products of the reaction then separate for the most part as reddish-brown oily drops, which collect at the bottom of the dish. The clear, colourless mother-liquor is poured off, and treated as shown later on.

The oil is now boiled with a large quantity of water for some time, and thereupon partially dissolves. The liquid is filtered hot and from the colourless solution white needles separate on cooling. These are

filtered off, and the mother-liquor utilised for again extracting the residual oil. This process is repeated until the solution no longer yields crystals on cooling. To this solution the colourless mother-liquor above mentioned is added.

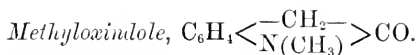


The crystalline product was first examined, with the following result:—

After a single recrystallisation from acetone, the substance was obtained in white, lustrous plates melting at 132—134°. It gave, on analysis, numbers which agree well with the formula  $\text{C}_9\text{H}_8\text{NBrO}$ , and is, therefore, as one would expect, monobromomethyloxindole.

It is soluble to some extent in hot water, scarcely at all in cold. It dissolves easily in alcohol, ether, and acetone, and crystallises best from the latter.

The bromine in this compound is very firmly combined. On boiling with caustic potash solution, it dissolves, but crystallises out unaltered on cooling.



The mother-liquor was then examined, being treated as follows:—

The solution is extracted 10 times with ether, the ethereal solution dried over calcium chloride, and the ether evaporated. The residue is an oil, which on standing for a short time solidifies to a beautiful, radiating, crystalline mass.

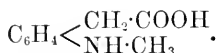
If this mass be now crystallised from water it is obtained in white, transparent needles, some of which are 4—5 cm. long. These, however, still contain 2—3 per cent. of the monobromo-derivative. To completely eliminate the bromine, the substance must be dissolved in hot water, and boiled for half an hour with zinc-dust and hydrochloric acid. This powerful reducing action has, however, also the effect of causing a considerable diminution in the yield.

The solution, after filtering off the zinc-dust, is extracted with ether as before, and the residual oil recrystallised from water. It is thus obtained in small, white needles, which, for analysis, were dried over sulphuric acid in a vacuum. The numbers obtained on analysis confirmed the supposition that the substance is methyloxindole. It melts at 86—88°, and volatilises slightly with steam. Heated by itself it distils with partial decomposition and formation of a reddish-brown substance. It is fairly soluble in hot water, but much less so in cold water and in light petroleum, easily in alcohol, ether,

acetone, and benzene. It is precipitated from its ethereal solution by light petroleum in fine oily drops, which solidify in a short time, forming beautiful transparent needles.

It does not combine with phenylhydrazine even on long-continued warming. This fact bears out the supposition that in dibromomethyloxindole the bromine-atoms are in the Pr 3-position.

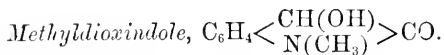
When boiled with caustic potash solution, it does not take up the elements of water, so as to form the corresponding acid,



It dissolves in the hot liquid, but is precipitated unaltered on cooling.

If bromine-water is added to an aqueous solution of methyloxindole, a crystalline precipitate is at once formed. This, however, is not identical either with dibromomethyloxindole or with monobromomethyloxindole, for it is quite insoluble in water and is not acted on by caustic potash solution. It seems probable, therefore, that the bromine is contained in the aromatic nucleus.

By the action of nitrogen trioxide on methyloxindole in dilute aqueous solution, a compound is formed which was found to be identical with methylpsendoisatinoxime. When prepared by this method, however, it is much more difficult to purify.



This compound is obtained by the reduction of methylpsendoisatin. The following method gives the best results:—

4 grams of dibromomethyloxindole are boiled with water for 2 to 3 hours. To the solution thus formed, which contains methylpsendoisatin and hydrobromic acid, zinc-dust is added, and the whole boiled till the liquid is colourless, more acid being added if necessary. The filtered and cooled solution is then extracted 20 times with ether. The residue left on evaporating the ether is always slightly yellow, part of the methyldioxindole being oxidised by the oxygen of the air to methylpsendoisatin.

This is twice recrystallised from benzene, and is thus obtained in the form of colourless needles or prisms. It must be dried over sulphuric acid in a vacuum, as it becomes slightly brown when heated for any length of time at 100°. Its analysis agrees well with the formula  $\text{C}_9\text{H}_9\text{NO}_2$ . It melts at 149–151° and decomposes on further heating. It is sparingly soluble in cold water, alcohol, ether, and benzene, but easily in the hot liquids. From water and alcohol, the

crystals are always yellowish, but it can, as above stated, be obtained white from its solution in benzene.

If the solution of methylindole is allowed to stand in the air it is gradually oxidised to methylpseudoisatin, but if it be made alkaline oxidation will proceed very rapidly.

One important difference is to be noted in the behaviour of isatin and methylpseudoisatin towards reducing agents. Isatin on reduction in alkaline solution yields isatyd, a compound containing a molecule twice as large as isatin, whereas methylpseudoisatin yields the same product as in acid solution, viz., methylindole.

The following table shows the derivatives of methylindole obtained up to the present time, together with the corresponding indole-compounds.

Indole, m. p. 52°; b. p. 245°.	Methylindole, b. p. 239°.
Oxindole, m. p. 129°.	Methyloxindole, m. p. 86—88°.
Bromoxindole (constitution unknown), m. p. 176°.	Bromomethyloxindole, m. p. 132—134°.
—	Dibromomethyloxindole, m. p. 204°.
—	Dichloromethyloxindole, m. p. 145—147°.
Dioxindole, m. p. 180°.	Methyldioxindole, m. p. 149—151°.
Isatin, m. p. 200—201°.	Methylpseudoisatin, m. p. 134°.
Isatinphenylhydrazone, m. p. 210°.	Methylpseudoisatinphenylhydrazone, m. p. 145—146°.
Isatinoxime, m. p. 202°.	Methylpseudoisatinoxime, m. p. 180—183°.

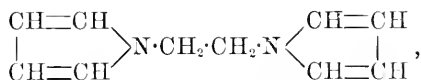
The above research was carried out in Professor Emil Fischer's laboratory at Würzburg, and I take this opportunity of expressing my best thanks to Professor Fischer for the kind advice and assistance given me throughout the investigation.

## II.—Action of Ethylenediamine on Succinic Acid.

By ARTHUR T. MASON, Ph.D., F.I.C.

MANY years ago, D'Arcet (*Annalen*, **16**, 215), by the action of ammonia on succinic anhydride, prepared succinimide, and, starting from this, Ciamician and Silber have, by means of phosphorus pentachloride, obtained tetrachloropyrrol (*Ber.*, **16**, 2398). Now, although this compound cannot be reduced in the ordinary manner to pyrrol, these investigators, availing themselves of Hepp's discovery that tetrachloropyrrol and tetrabromopyrrol can be easily converted into tetra-iodopyrrol by treatment with potassium iodide in alcoholic solution, found they had at their disposal a compound which by reduction with zinc-dust and potassium hydrate, gave pyrrol with the greatest ease, thus completing by stages the same synthesis which is effected directly by distilling succinimide with zinc-dust containing hydroxide.

The experiments about to be described were undertaken in the hope of arriving, by similar reactions, at an ethylenedipyrrol of the following constitution:—

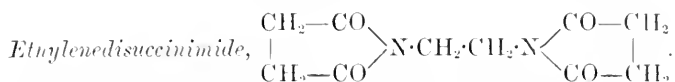


and although hitherto I have been unsuccessful in my object, I take the liberty of laying the results already obtained before the Society in order to secure this field of work, as well as that with the aromatic diamines which I have already begun. Succinic acid dissolves easily in an aqueous solution of ethylenediamine with evolution of heat and formation of the addition product  $(\text{CH}_2 \cdot \text{COOH})_2 \cdot (\text{CH}_2 \cdot \text{NH}_2)_2$ ; and as this has not, to my knowledge, been hitherto described, I take this opportunity of mentioning it. It is easily soluble in water, and crystallises therefrom in thick, white prisms. It melts at  $181$ – $182^\circ$  to a colourless liquid, giving up water and becoming semi-solid again. It is insoluble in alcohol and ether. An analysis of the substance dried at  $100^\circ$  gave the following numbers:—

0.2175 gram gave 0.1593 gram  $\text{H}_2\text{O}$  and 0.3235 gram  $\text{CO}_2$ .

0.1738       ,,       24.8 c.c. moist nitrogen at  $18^\circ$  and 718 mm.

	Calculated for $\text{C}_6\text{H}_{14}\text{N}_2\text{O}_4$ .	Found.
C. ....	40.45	40.56
H ....	7.86	8.13
N ....	15.73	15.55
O ....	35.95	—



This compound is formed when the addition product just described is heated above its melting point, water being eliminated: it is, however, by no means necessary to isolate the addition product in the pure state in order to obtain the best results. After preparing considerable quantities, I have no hesitation in giving the following as the most advantageous method:—

60 grams of succinic acid are mixed with 20 grams of ethylenediamine hydrate, and just sufficient water is added to bring the whole into solution on warming. The mixture is now heated in a flask over a small flame, with a thermometer in the liquid. As the water evaporates, the temperature gradually rises, and the heating is continued until the thermometer indicates  $195^\circ$ , when the whole has changed to a clear pale-brown syrup. After the temperature has reached  $180^\circ$ , the thermometer rises rapidly, and, if not carefully watched, overheating may occur, which, curiously enough, has an influence on the yield, although the pure product can be distilled without decomposition. On cooling, the whole crystallises to a mass of prismatic needles, which is almost white; this is recrystallised from about 800 c.c. of water, when 40 grams of a practically pure product are obtained in thick, white, prismatic needles which melt at  $250\text{--}251^\circ$ . It distils almost without decomposition at about  $395^\circ$ , and sublimes in long, colourless, prismatic needles—the sublimate being highly electrical. On distillation with zinc-dust containing hydroxide, the pyrrol reaction with pinewood was easily obtained, but the compound could not be isolated in quantity sufficient for an accurate investigation of its properties. The di-imide was dried at  $120^\circ$  for analysis; the following are the numbers obtained:—

0.2215 gram gave	0.114 gram water and 0.429 gram carbon dioxide.
0.1625        „	0.0816        „        „        0.3192        „        „
0.1714        „	18.5 c.c. moist nitrogen at $14^\circ$ C. and 726 mm.
0.1565        „	17.5 c.c.        „        „ $15^\circ$ C.        „        719        „

		Found.	
Calculated for		I.	II.
$\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_4$ .			
C. ....	53.57	52.82	53.57
H. ....	5.35	5.71	5.57
N. ....	12.50	12.10	12.41
O. ....	28.57	—	—

It is soluble in hot water, but only sparingly in cold; boiling alcohol dissolves traces of the substance, whilst in ether, benzene, acetone, and

light petroleum it is altogether insoluble. The substance is not attacked by bromine and water at  $120^{\circ}$ , but if heated in sealed tubes for three hours at  $180^{\circ}$  in the proportions of 1 mol. of substance to 4 mols. of bromine, the whole of the bromine is absorbed, and the tubes on cooling are filled with a pale-brown scaly product, there being at the same time a large pressure in the tubes due to carbon dioxide and monoxide.

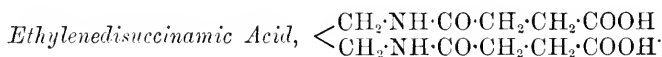
The brown scales, on washing with alcohol and ether, became white, and on analysis gave numbers closely agreeing with those required for ethylenediamine bromhydrate:—

0.2974 gram gave	0.1251 gram water and 0.1231 gram carbon dioxide.
0.2078       ,,	24 c.c. moist nitrogen at $25^{\circ}$ C. and 721 mm.
0.1925       ,,	0.3257 gram silver bromide.

	Calculated for $C_2H_4(NH_2)_2 \cdot 2HBr$ .	Found.
C .....	10.81	11.22
H .....	4.50	4.67
N .....	12.61	12.20
Br. ....	72.07	72.00

Besides this, a sample of pure ethylenediamine bromhydrate was prepared from the pure base, and when compared, the two preparations agreed in all particulars. The formation of brominated succinic acids was not observed, but as only two atoms of bromine are required by the bromhydrate, and as a large pressure, due principally to oxides of carbon, was found in the tubes, we have probably to do with a more complete decomposition with formation of brominated ethanes.

The action of the halogens on ethylenedisuccinimide, as well as on analogous compounds belonging to the aromatic series, in the absence of water, will be treated of in a subsequent paper.



In the preparation of this substance, 22.4 grams of the di-imide are pulverised and dissolved in hot water, and a solution of about 20 grams of pure barium hydroxide added. The whole is then kept boiling for about 10 minutes, and the excess of baryta precipitated by a stream of carbon dioxide. In the still warm filtrate, the combined barium is carefully precipitated by the theoretical quantity of dilute hydrogen sulphate, using a trace of Orange III (sodium salt of dimethylanilineazobenzenesulphonic acid) as indicator. When all the barium has been precipitated, the mixture is allowed to stand on the water-bath for two or three hours, filtered, and evaporated to about



one quarter of its original volume. After standing several hours in a cold place, the solution begins to deposit the new acid in the form of large, colourless, quadratic plates, having the constant melting point  $184-185^{\circ}$ . For analysis, it was recrystallised from water, and dried at  $100^{\circ}$ ; the following are the results obtained:—

0.1647 gram gave 0.099 gram  $H_2O$  and 0.2768 gram  $CO_2$ .

0.1735        „        0.1007        „        „        0.2925        „

0.1415        „        14.1 c.c. moist nitrogen at  $22^{\circ} C.$  and 726 mm.

	Calculated for $C_{10}H_{14}N_2O_6$ .	Found.	
		I.	II.
C.....	46.15	45.83	45.97
H.....	6.15	6.67	6.44
N.....	10.76	10.76	—
O.....	36.94	—	—

The new acid is easily soluble in hot water, with greater difficulty in cold. It dissolves in hot alcohol with tolerable ease, but is only sparingly soluble in cold, and is insoluble in ether, benzene, acetone, and light petroleum.

In the presence of even very dilute mineral acids, it gives up water on heating, being converted into the di-imide described above. Neither hydrazone nor isonitroso-derivative could be prepared by the action of phenylhydrazine and hydroxylamine, and this was expected, as it has already been proved in many cases that compounds containing the “carbonyl” group  $CO$ , between carbon and nitrogen, do not react like true “ketones.”

*Silver Salt*,  $C_{10}H_{14}N_2O_6Ag_2$ .—The silver salt is prepared in the usual way by dissolving the acid in aqueous ammonia, evaporating till the excess of the latter has disappeared, and precipitating the solution in water with silver nitrate. It falls as a voluminous, white precipitate, easily soluble in ammonia, but insoluble in the general solvents. It darkens rapidly on drying at  $100^{\circ}$ , but is stable in diffused sunlight. A silver estimation was made.

0.1647 gram gave 0.09886 gram silver chloride.

	Calculated for $C_{10}H_{14}N_2O_6Ag_2$ .	Found.
Ag.....	45.57	45.17

*Calcium Salt*,  $C_{10}H_{14}N_2O_6Ca + 3H_2O$ .—Prepared from the di-imide by heating with the theoretical quantity of pure calcium hydrate suspended in water. The solution is filtered, evaporated on the water-bath, and then allowed to stand over sulphuric acid; the salt

separates in large, prismatic crystals containing 3 mols.  $\text{H}_2\text{O}$ . The calcium estimation gave the following result:—

0.2280 gram gave 0.0362 gram calcium oxide.

0.1569        „        0.0245        „        water.

	Calculated for $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_6\text{Ca} + 3\text{H}_2\text{O}$ .	Found.
Ca .....	11.36	11.34
$\text{H}_2\text{O}$ .....	15.34	15.61

*University Laboratory,  
Zürich.*

### III.—*The Principles of Thermochemistry.*

By SPENCER UMFREVILLE PICKERING, M.A.

THE connection between a chemical action and the heat evolved therein is a question of vital importance to all chemists and physicists, yet the fundamental principles on which it depends are at present in an eminently unstable and unsatisfactory condition. On the one hand, it is acknowledged that the atoms possess a certain amount of potential energy or affinity which becomes partially or entirely saturated when they combine together, and which, in its saturation, must, according to the principles of physical science, evolve an exactly equivalent amount of kinetic energy, or, in the calorimeter, heat,\* while, on the other hand, the heat evolved in a reaction is not yet recognised as a measure of the affinities saturated, and there are thousands of instances known in which the saturation of these affinities apparently results in a paradoxical absorption of heat.

In 1853. Thomsen (*Pogg. Ann.*, 92, 34, and *Ber.*, 6, 425) stated that “every simple or complex action of a purely chemical character is associated with a production of heat.” Naumann in 1869 (*Lieb. Ann.*, 151, 158) stated that “with few exceptions, capable of being otherwise explained, those chemical changes which must take place with an absorption of heat are, so to speak, indirect changes. That is to say, they occur simultaneously, and are dependent upon other changes which are themselves accompanied by a production of heat.”

\* Unless we assume the existence of some form of kinetic or potential energy which has hitherto escaped our observation, an assumption which we are scarcely justified in making, even when all other possible explanations fail.

While Berthelot in 1879 (*Méc. Chim.*, 2, 421) thus enunciated his more emphatic and comprehensive *Principe de travail maximum*: "Every chemical change which is completed without the intervention of external energy will always tend towards the production of that body, or that system of bodies, developing the maximum quantity of heat," adding, as a corollary, that "every chemical reaction capable of occurring without the previous expenditure of work, and without the intervention of external energy, necessarily occurs, if it develop heat."

No one can study the mass of thermochemical data which exist without concluding that such statements cannot be very far from the truth, at the same time we must agree with L. Meyer (*Modern Theories*, 429) in considering that Berthelot's explanation of many endothermic reactions is decidedly forced; for to explain reactions occurring in solution, he has to refer them to the heat of formation of the anhydrous molecules, thus ignoring the chemical nature of solution, of which, however, he is a firm supporter; nor does he attempt any explanation of the heat absorbed when many strong solutions are diluted, a chemical action, again, according to his views.\*

But when we examine the wording of Berthelot's principle more closely, we see that the expression "tends towards" destroys the whole value of the statement, and affords a loophole for explaining (?) away any discordant facts, whereas if "produces" be substituted for "tends towards the production of" the statement must be met with an absolute denial: hydrogen and oxygen do not combine at 0°, though they would develop heat in so doing; water decomposes at 2000°, absorbing heat; and endothermic compounds are often, when formed, quite stable.

On still wider grounds, however, we must reject any principles, such as those of Berthelot and Thomsen, the gist of which lies in a distinction between physical and "purely chemical" action, a distinction which never has been possible, and which is every day becoming less possible.

The whole of the thermal results in any action must be explained on one and the same principle.

\* Meyer's objection to Berthelot's principle on the ground that it is applicable to bodies at the absolute zero only, is based, I think, on an unfair interpretation of what Berthelot meant by heat being an external energy; similarly, his objection on the score of the heat of neutralisation bearing evidence opposed to that of the "avidity" of acids, is entirely due to his misconception of the quantities measured in neutralisation; the heat of neutralisation affords, as a matter of fact, stronger evidence than any yet obtained of the direct proportionality of the heat evolved to the affinity saturated (*Trans.*, 1887, 593). For a criticism of some of the explanations of endothermic actions given by Berthelot, see Rathke, *Ueber die Principien der Thermochemie*, Halle, 1881.

In seeking for such a principle, we must start with obtaining a clear conception of the facts to which this principle must apply. On the one hand, it is a fact that substances will not combine until a certain temperature be reached, even though their combination at lower temperatures would be accompanied by an evolution of heat; while, on the other hand, it is also a fact that, when the temperature of any body is raised to a certain point, it decomposes whether its decomposition be attended with an absorption or an evolution of heat, this being probably true even of the elementary molecules themselves. Thus, the conversion of the potential energy of affinity into kinetic energy (heat) occurs only above a certain definite temperature, different for each different body, and this kinetic energy becomes converted back again into affinity at some higher temperature; but we know far too little about atomic motions to attempt any explanation of how these temperatures are conditional in each special case. We must content ourselves with the fact that combination occurs between certain limits of temperature only.

The phenomena which we have to explain are, therefore, confined to those accompanying actions which do actually occur, and the only principles which we can attempt to enumerate are those which determine whether a certain reaction will occur provided the temperature be between the limits at which it is possible, and to determining which out of several possible reactions will occur.

The accepted principles of dissociation, the chemical nature of solution, and the teaching of the thermal results of neutralisation, will, I believe, afford grounds sufficient for the foundation of such a principle.

Inasmuch as combination is the result of the saturation of affinity, and the saturation of this affinity must always liberate a corresponding amount of heat, it is evident that *every act of combination must cause an evolution of heat, and that in any reaction where heat is absorbed this absorption must be due to some accompanying decomposition.*

But as decomposition cannot be the direct result of affinity, it must be due to the fact that some of the substances present are, at the temperature of the reaction, above that temperature at which they begin to dissociate. This dissociation, moreover, cannot be that of any of the products, for even if the products were entirely dissociated back again into the reagents, this would be tantamount to no combination of the reagents having occurred, and hence the minimum value of the heat evolved would be *nil* and not a negative quantity.\*

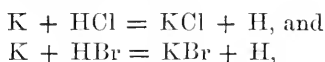
\* Heat would be absorbed if the compound dissociated into substances simpler than the reagents themselves; if, for instance,  $\text{KCl}$  combines with water to form a hydrate which when formed dissociates partially into  $\text{K}$  and  $\text{Cl}$ , &c.; but such a case is, I think, impossible. If the more saturated hydrate dissociated into  $\text{K}$  and

Any dissociation occurring must, therefore, be that of the reagents. Hence, "*in every endothermic reaction one or more of the reagents must be in a partially dissociated condition.*"

Moreover, *when combination occurs, it will occur independently of whether it involves subsequent absorption of heat through the removal of the products of dissociation, and the consequent necessity for the occurrence of further dissociation.* It is obvious that the affinity of the reacting substances, and not the subsequent consequences of their reaction, can alone determine whether they shall react or not.

It also follows as a matter of necessity, I think, *that in any complex system of atoms, where two or more arrangements are possible and where the various products remain within the sphere of action, capable of further interaction, where such interaction is possible, (that is, where the temperature is within the limits above mentioned), those products, the formation of which is attended with the greatest evolution of heat, will be formed to the exclusion of the others.*

Thus, in illustration of my meaning, if potassium be brought into the presence of excess of hydrochloric and hydrobromic acids in aqueous solution, the two actions—



are both known to be possible, and it is also known that the KCl and KBr formed remain in the solution, capable of reacting with any excess of HBr and HCl respectively; in such a case, my proposition states, the potassium will be converted entirely into chloride or bromide according as the gross heat of formation of one or other of these salts is the greater.\*

Before enquiring as to how far the principles are supported by known facts, and how endothermic reactions may be explained in accordance with them, we must point out that those endothermic reactions which are brought about by the so-called concurrence of another exothermic reaction, require, in reality, no special explanation, the endo- and exo-thermic reactions forming, in reality, but one action. Thus, copper will not dissolve in weak sulphuric acid, the action being endothermic, but zinc does dissolve, the action being exothermic; yet when alloyed with zinc, copper dissolves in the acid, the action being

Cl, *à fortiori*, the less saturated anhydrous salt would do so also, and the dissociation products of the hydrate would, therefore, not be simpler than the reagent.

\* Some of both salts would, no doubt, be formed in the first instance, but the one which was formed with the least evolution of heat would be eventually entirely converted into the other, this reaction being, *ex hyp.*, one of those which does occur, and which, having once taken place, could not be reversed without an absorption of heat.

accompanied with an evolution of heat. But this is not really a case of the *copper* dissolving, but of a compound of copper—*brass*—dissolving, and since brass is capable of dissolving with an evolution of heat, it is but in accordance with general observation to find that it does so.

As true solids do not react with each other, the cases to be examined are those in which gases or liquids figure. The reactions indicated below are the chief reactions in which gases are concerned, and which are endothermic at  $18^{\circ}$ .

$\text{H}_2\text{O}, \text{O}, \text{aq.}$	$\text{HCl}, \text{aq.}, \text{O}_3.$
$\text{Cl}_2, \text{O.}$	$\text{Br}_2, \text{O}, \text{aq.}$
$\text{N}_2, \text{O.}$	$\text{Br}_2, \text{O}_5, \text{aq.}$
$\text{N}, \text{O.}$	$\text{HBr}, \text{aq.}, \text{O}_3.$
$\text{N}, \text{O}_2.$	$\text{Cl}_2, \text{O}_5, \text{aq.}$
$\text{N}_2\text{O}, \text{O.}$	$\text{C}_2, \text{Cl}_4.$
$\text{N}_2\text{O}, 2\text{H}_2\text{O} (= (\text{NH}_4\text{NO}_3)).$	$\text{C}_2, \text{H}_4.$
$\text{N}_2, 2\text{H}_2\text{O} = (\text{NH}_4\text{NO}_2).$	$\text{C}_2, \text{H}_2.$
$\text{C}_2, \text{N}_2.$	$\text{C}_2, \text{H}_2, \text{N}_2.$
$\text{C}, \text{N}, \text{H.}$	$\text{C}, \text{S}_2.$
$\text{SO}_2, \text{aq.}, \text{S.}$	$\text{CO}_2, \text{C.}$
$\text{H}, \text{I.}$	

This list affords a striking argument in favour of the above principles, for not one of these reactions is capable of taking place at ordinary temperatures. One or two of them occur directly at higher temperatures ( $\text{C}, \text{S}_2$ ;  $\text{C}_2, \text{H}_2$ ), but at these temperatures they are probably exothermic, at any rate, our imperfect knowledge of the heat capacity of the bodies concerned is not sufficient to enable us to affirm that they are not so. In the case of  $\text{CO}_2 + \text{C} = 2\text{CO}$ , the reaction which takes place at  $600^{\circ}$  is no doubt endothermic at that temperature, and affords one of the simplest illustrations of the satisfaction of affinity producing endothermic results *indirectly*, owing to the dissociation of the reagent. Thus, at  $600^{\circ}$  carbon dioxide is partially dissociated, that is, the stable condition of a mass of that gas is  $x\text{CO}_2 + (1-x)\text{CO} + (1-x)\frac{1}{2}\text{O}_2$ , and, if either of these three substances be removed, the amount of dissociation will be increased or diminished till this stable condition be reproduced. Carbon being capable of combining with the free oxygen at this temperature, evolving 28,000 cal. in so doing, removes this oxygen, and necessitates the liberation of a fresh supply by the further dissociation of the dioxide, and so on till this latter has been entirely decomposed, a decomposition which absorbs 68,000 cal., leaving the algebraic sum of the actions at  $-40,000$  cal.\*

\* Referring to this action, Rathke states that he considers it possible that the

No real difficulties arise till we come to consider cases in which liquids are chiefly concerned, and the three most difficult classes of such cases are the following :—

- (1.) The endothermic results on dissolving solids in liquids.
- (2.) The endothermic results on diluting strong solutions.
- (3.) The endothermic results attending double decomposition between substances in solution.

Neither the immediate nor the mediate source of the absorption of heat which occurs when many salts are dissolved in water (to take a concrete instance of a solid and solvent) have ever been elucidated. It is just as insufficient to say that it is due to the fusion of the solid as to say that this is a physical action, and, therefore, requires no explanation. As a matter of fact, the heat absorbed cannot possibly be accounted for by the fusion of the solid. The absorption amounts in many cases to some 10,000 cal. per equivalent of salt,\* and this represents but a portion, possibly but a half, of the total value of the endothermic action, for it is always counterbalanced to a greater or less extent by the heat evolved in the formation of the hydrates of which the solution is composed.

The heat of fusion of very few salts has been determined, and to calculate its heat of fusion at the ordinary temperatures at which it is dissolved, it is necessary to know not only its heat of fusion at the temperature at which fusion naturally occurs, but also its heat capacity (specific heat) in the liquid and solid state. Potassium and sodium nitrates are the only anhydrous salts for which we have these data, but, judging by a comparison of these salts with other bodies, their heat of fusion is not abnormally small, yet it amounts to only—

$$\begin{aligned} -(5300 + 3849) &= -1451 \text{ cal. for NaNO}_3 \text{ at } 18^\circ, \\ -(4800 + 2678) &= -2122 \text{ „ for KNO}_3 \text{ „} \end{aligned}$$

quantities wholly insufficient to explain the heat absorbed in the dissolution of the salts at  $18^\circ$ , which is  $-5000$  and  $-8543$  cal. respectively. Moreover, we have a still more fatal objection in the fact that the heat absorbed in dissolving a salt *increases* rapidly as the temperature is lowered,† whereas the heat absorbed in its fusion *diminishes* with a fall of temperature.

presence of the second reagent may of itself induce dissociation of the first one. This amounts to the inadmissible conception of the satisfaction of affinity producing *directly* a further supply of affinity, that is, an endothermic reaction occurring in which affinity is the only agent. The whole virtue of dissociation in producing endothermic results consists in the presence of a third body (the product of the dissociation) capable of reacting with the other reagent; till some of this third body is present, no such reaction can take place.

\* I refer, for the sake of simplicity, to anhydrous salts only.

† This increase cannot be due to a diminution of heat evolved in the formation of

But when a salt is dissolved in excess of water it becomes far more disintegrated than when it is merely fused. When fused, the molecules are within the sphere of each other's attraction, and are indeed, I believe, combined to form molecular aggregates, but this cannot be the case when they are separated from each other by several hundred molecules of the solvent; they are then as much beyond the sphere of each other's attraction as if they were in the gaseous condition; indeed, insisting, as I think we must do, on the continuity of the liquid and gaseous conditions,—a continuity which has so often been urged against the hydrate theory of solution, but which, as a matter of fact, is of vital importance to that theory,—we must acknowledge that the condition of a substance dissolved in excess of water is *identical* with that of its vapour at the same temperature, and to separate the molecules from each other to the same extent, whether the condition be the dissolved or the ordinary gaseous condition, must absorb the same amount of heat. Thus we have not only the heat of fusion of the solid, but also its heat of volatilisation as a source of absorption of heat, and the sum of these two quantities would certainly be amply sufficient to account for the absorption noticed on dissolution,\* being, in those cases where data are known, ten or twenty times greater than the heat of fusion alone; and, moreover, it is a quantity which *increases* as the temperature falls, precisely what is noticed in the heat absorbed in dissolution.

Thus, the heat of fusion of  $\text{Br}_2$  is  $-380$  cal. at  $18^\circ$ , and diminishes by  $4.8$  cal. for every fall of  $1^\circ$ ; the heat of volatilisation is  $-7562$  cal., increasing  $11.3$  cal. for a fall of  $1^\circ$ .

The sum of these two is  $-8032$  cal., increasing by  $6.5$  cal. for a fall of  $1^\circ$ .

In the case of water—

$$\text{Heat of fusion at } 18^\circ = -(1580 + 8.64(t - 18)).$$

$$\text{Heat of volat. at } 18^\circ = -(10798 - 12.05(t - 18)).$$

$$\text{Sum at } 18^\circ \dots\dots\dots = -(12378 - 3.41(t - 18)).$$

Having thus traced to its source the absorption of heat which occurs during dissolution, the next question is, what forces exist sufficient to bring about such endothermic results? As previously stated they must be due to the dissociation of the reagents,—the salt

the hydrates: these hydrates are *less* dissociated at lower than at higher temperatures, and the heat of complete formation of any particular hydrate is probably influenced but very little by temperature, at any rate this is so with the formation of solid hydrates, as I have shown (Trans., 1887, 335).

\* The heat of volatilisation in such a case would be  $580$  cal. less than it is when the substance is vaporised in the usual way, since this amount of heat is absorbed in the external work of expansion in the latter case.



or the water. Dissociation of the salt may occur to a certain extent in the case of hydrated salts, but it is scarcely worth enquiring further into its influence, since it will not help us to explain other cases; it must, therefore, be the dissociation of the water which acts as the primary cause.

On views which I and others have for some years been pressing, all liquids and solids must be regarded as consisting of compounds or aggregates of the fundamental molecules, these aggregates, just like the hydrates in a solution, being more or less dissociated, and being reduced to less complex ones as the temperature rises; and the recognition of these aggregates can alone give a satisfactory explanation of the physical properties of matter in its three conditions.

Thus: in true gases such aggregates, as the vapour-density tells us, do not exist, and from gases we learn that the heat capacity of each atom is a constant quantity.\* With solids as with imperfect gases, the heat capacity, though very nearly the sum of the atomic heats, is not exactly so, and, with solids, increases slightly with the temperature; this is exactly what would occur if the solids consisted of dissociating aggregates: the heat absorbed by the dissociation renders the apparent heat capacity greater than it is with gases, and as the aggregates dissociating become less complex, and, therefore, more firmly united, as the temperature is higher, more heat will be absorbed in their decomposition, and hence the apparent heat capacity of the solid will increase. But this variation in the heat capacity of solids will not be very great, since the stability of solid particles is unfavourable to dissociation; when, however, we come to liquids, where the particles are less restrained in their motions, dissociation will take place to a much greater extent, and we find, as a consequence, that the heat absorbed in this dissociation is so great that it not only renders the apparent heat capacity of a liquid much greater than that of the corresponding solid or gas, but that it makes it increase so rapidly with a rise of temperature, and produces such irregularities in the increase, that no approach to any so-called law can be observed here. As the boiling point is approached, the absorption of heat generally becomes much greater, and, under ordinary atmospheric conditions, an almost sudden absorption (heat of vaporisation) occurs at this point when the simplest possible aggregates are resolved into their fundamental molecules. The irregularities observed in the expansion and other physical properties of many liquids can also be explained only on the supposition of a discontinuous action, which is wholly inconsistent with the idea of the fundamental molecule being

\* But not the same in the two cases. With gases 2·4, and with solids 6·4, is the heat capacity of each atom.

the acting unit of a liquid.\* The continuity of the liquid and gaseous conditions is strictly adhered to according to this view, and the heat of volatilisation of a liquid at any temperature (less the heat absorbed in producing the expansion) is simply the heat of decomposition of the liquid aggregates existing at that temperature into the fundamental molecules.

Every physical fact relative to water tends to show that its composition in the liquid condition is pre-eminently complex, and its heat of volatilisation tells us that at  $18^{\circ}$  (for instance) the heat of formation of the water aggregates is as much as 10,000 cal., approximately.†

It is argued that the so-called determinations of the molecular weights of solids and liquids by measuring the extent to which they lower the freezing point of some solvent (Raoult's method), proves that these molecular weights are of a very simple character. But these results, which are inconsistent with so many other facts, receive an easy explanation on my views as to the nature of dissolved substances. Raoult's method applies only to dilute solutions, and in these dilute solutions the substance is really in the gaseous condition, and we are determining the molecular weight not of the solid or liquid but of the gas.‡

Now according to the kinetic theory of gases, which in this respect applies equally to all fluids, a mass of water consisting of aggregates having the average composition of  $x\text{H}_2\text{O}$  at a temperature of  $18^{\circ}$ , is made in reality of aggregates some at a temperature above  $18^{\circ}$ , some at a temperature below  $18^{\circ}$ ; those aggregates which are at the higher temperature will be dissociated into less complex aggregates than

\* All that is said of the heat capacity may, indeed, be said of the expansion of substances. Perfect gases, where no dissociation occurs, expand regularly; in dissociating gases the expansion increases rapidly; in solids, where but little dissociation is possible, the expansion is comparatively constant, whereas in liquids, where dissociation may occur to a large extent, the expansion increases rapidly, and often irregularly. It may be suggested that the peculiarities in the expansion are the causes of those in the heat capacity, but this still leaves us with the equally difficult problem of explaining the former. It is far more probable that they are both consequences of dissociation.

† Taking the mean heat capacity of 18 grams of water between  $18^{\circ}$  and  $100^{\circ}$  as 18.1, and that of steam at constant volume as 6.65, and the heat of volatilisation of 18 grams of water at  $100^{\circ}$  as 9650 cal., we get  $[9650 + 82(18.1 - 6.65) =]$  10,589 cal., as the heat of volatilisation at  $18^{\circ}$ , of which 580 cal. are absorbed in producing the accompanying expansion. The correctness of this value, however, is doubtful, as the heat capacity of steam below  $130^{\circ}$  has not been determined; but an error of even several thousand calories would not affect the present argument.

‡ Ramsay (Trans., 1888, 623) found the method applicable to nitrogen tetroxide when dissolved in only 18 mols. of acetic acid; but in this case the vaporisation of the tetroxide due to its dilution would be materially increased by the temperature of the determination being only  $10^{\circ}$  below its normal boiling point.

$x\text{H}_2\text{O}$ , say,  $m\text{H}_2\text{O}$ ,  $m_1\text{H}_2\text{O}$ , &c., whereas those at the lower temperature will be more complex, say,  $z\text{H}_2\text{O}$ ,  $z_1\text{H}_2\text{O}$ ; at this particular temperature, therefore, the stable condition of a mass of water is such that there is a certain number of  $x$ ,  $m$ , and  $z\text{H}_2\text{O}$  aggregates present, and if any of these be removed from the sphere of action, more dissociation or combination will take place till this stable condition be restored.

In fact, the water at this temperature is continually giving off fundamental molecules (that is, has a vapour-tension), a certain number of these fundamental molecules must be present in the mass of the water, and these molecules possess a potential energy equivalent to 10,000 cal. greater than that of the average particles constituting this mass, and these particles will be able to effect a combination with *evolution* of heat, which in the case of the average particles would involve the *absorption* of some 10,000 cal., and, therefore, be impossible.

One fundamental water molecule coming in contact with a salt molecule would thus be capable of combining with it if the heat of volatilisation of the salt molecules was not greater than 10,000 cal.: the simultaneous arrival of two such water molecules would combine with the salt if its heat of volatilisation were double this quantity; but it is not necessary even to have recourse to this simultaneous arrival even in such cases, for the combination of the salt molecule with one molecule of water only would not remove the former entirely from the sphere of attraction of its fellows, it would not be completely volatilised, and would not require to be supplied with as much as its full heat of volatilisation.

The free water molecules being thus removed by their combination with the salt from the sphere of action, other water aggregates must, according to the laws of dissociation, split up to supply the vacancies, and this action is accompanied by an absorption of — 10,000 for every 18 grams thus dissociated. But, if this absorption of heat were not subsequently counterbalanced, we should have proved far too much. In the cases which have been investigated, it has been found that each salt molecule combines ultimately with over  $100\text{H}_2\text{O}$ ; the heat absorbed in liberating this  $100\text{H}_2\text{O}$  would be 1,000,000 cal., not to mention the heat absorbed in the volatilisation of the salt, and it is quite impossible to imagine that the heat of combination of the water and salt molecules is so great as to nearly, and often indeed, more than counterbalance such an absorption.\* But here the teaching of the heat of neutralisation comes to our aid; we learn from it, as I have shown (Trans., 1888, 872), that the affinity which binds the dissolved molecules to those of the solvent does not affect that by which

\* The heat developed in the mere combination of each water molecule with a salt molecule is probably between 200 and 5000 cal.

the solvent molecules are united with each other; in dilute solutions, the water molecules are just as much combined with each other as they are in a mass of pure water, the hydrates present are compounds of the salt with the aggregates or polymers of  $H_2O$ ; and thus when a solid is dissolving, as the proportion of the water molecules in the hydrate increases, these then recombine with each other, and in doing so will, of course, evolve the same amount of heat that their production from the water aggregates absorbed. The net results obtained, therefore, when dissolution is complete, will simply be the algebraic sum of two quantities: (1) the heat evolved in the combination of the salt and water molecules, (2) the heat absorbed in volatilising the salt molecule; and according as the former or latter of these is the greater so will the heat of dissolution be positive or negative; but the motive power, if I may use such a term, which produces these results is the energy contained in the free water molecules.

When a salt is dissolved by admixture with ice, the heat absorbed is greater by the heat of fusion of the ice than in the case of water, but the same explanation will be sufficient in this case also. Ice near its melting point is certainly in a state of incipient fusion; and some of the particles of liquid water present in it are certainly dissociated, even as far as the fundamental molecules, as is proved by the considerable vapour-pressure of ice at this temperature. We, therefore, have the same motive power as in the case of water. It may be predicted, however, that no such action would occur if the ice were perfectly dry, as it is at a temperature some degrees below zero, and it is certain that no such action could take place if the temperature were below that of the formation of the so-called cryohydrate.

The endothermic results noticed in many cases when strong solutions are diluted are but the extension of the action primarily occurring when the salt is dissolved. As the dilution is increased, the hydrates become higher and less dissociated, evolving heat, while the salt becomes more entirely volatilised, absorbing heat, and the sign of the thermal change depends on the relative value of these two actions. Some years ago (*Chem. News*, 54, 217) I was led to believe in the existence of two such opposite actions, from the mere study of the curves representing the heat of dilution as given by Thomsen.

Another endothermic reaction also undoubtedly occurs in many cases—the dissociation of a salt into its free acid and base. This, I think, is a purely mechanical action, operating in the following manner. The salt in question, when liquid, is somewhat unstable and partially dissociated at the existing temperature, even when no water at all is present, and the extent of this is limited by the chances which occur of the dissociated components meeting each other when in a suitable condition and recombining, and these chances of

meeting are diminished a hundredfold when we increase a hundred times the space over which the substance extends by diluting it. The amount of dissociation occurring would thus be directly proportional to the volume of the liquid, and Thomsen's results with acid sulphates (*Thermochem.*, 3, Plate VI) tend to support this view.\* On such a view, dilution could never start, but only increase dissociation, and we have no grounds for supposing it to be otherwise.

The third important class of enthalpimic reactions to be explained is that in which double decomposition occurs between two dissolved substances. Double decomposition between two salts presents us with an instance of most frequent occurrence, and to investigate this we may go to the root of the matter by ascertaining how and on what principles a base divides itself between excess of two different acids.

According to the deduction drawn above from theoretical considerations, the acid which evolves the most heat on neutralisation will take the whole of the base, and, consequently, if both acids have the same heat of neutralisation, as is generally the case when excess of water is present, they will each take the same amount of the base, this referring only to cases where the salts formed are stable and remain in solution, and it being assumed, of course, that the acids are present in equivalent proportions. When the acids are not present in equivalent proportions the base will divide itself between them in proportion to the number of equivalents of each present; the division being regulated simply by the chances of impact.

This is nothing but the law enunciated by Berthollet in 1803, and discarded at the present time as being altogether insufficient. But I think that it will yet be found sufficient while the more elaborate theories of recent days will fail.

In cases where one of the salts formed is partially dissociated, the stable salt will be formed to the exclusion of the dissociated one when the solvent water is very large; but if the water is not in large excess there will be a limit to the dissociation and some of the less stable salt will be formed. For, the salt being dissociated, means that at the given temperature its condition of stability is  $xAB + (1-x)(A + B)$ , ( $A$  and  $B$  being the acid and base which form it); the free base  $B$  coming in contact with and combining with the stronger acid,  $A'$ , is thus removed from the sphere of action, and more of the salt  $AB$  dissociates to give a further supply

\* There are of course other actions occurring besides the dissociation of the salt as the dilution proceeds; we should not therefore expect the action to be represented by a straight line, but by lines which more nearly approach straightness than they do in cases where these other actions are the only ones occurring, as in the case of diluting stable salts. Such are the characters of the curves in the two cases.

of free base, and this action must continue as long as any dissociation at all takes place. But, the proportion of the free weak acid present increasing, a point will be reached when every molecule of AB will find itself within the sphere of action of so many molecules of this acid, that there would always be one of these present in a suitable condition to recombine with the base B the instant it dissociates from its former acid molecule. Practically, there would be no longer any dissociation under these circumstances. By separating the salt AB farther from the free acid, an increase in the proportion of water present would increase the limits of dissociation, and, therefore, also the proportion of stable salt formed. It is obvious also that this latter would be increased by adding more of the stronger acid, and diminished by more of the weaker one.

All the determinations which have been made of the division of base between two acids by thermal methods depend on the comparison of the action of an acid on the base with that of sulphuric acid on the same base. The latter action is therefore of paramount importance.

Supposing in the first place that the heat of neutralisation of  $\text{H}_2\text{SO}_4$  per H displaced is the same as that of HCl and  $\text{HNO}_3$  (a supposition which I shall shortly justify), then when 4NaOH is mixed with 4HCl and  $2\text{H}_2\text{SO}_4$ , the system formed, according to the principles of division of the base which I have laid down, would be 2NaCl and 2HCl,  $\text{Na}_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4$ ,—an equal division. But, as a matter of fact, whatever the explanation of the fact may be (and the explanation will be given below),  $\text{Na}_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4$  react on each other and form the acid salt  $2\text{NaHSO}_4$ , thus leaving no free sulphuric acid, and an alteration in the division of the base would, therefore, become necessary in order to supply the place of the free sulphuric acid thus removed. In fact, sulphuric acid acts as a monobasic acid only, in this reaction, and consequently we should compare 4HCl with  $4\text{H}_2\text{SO}_4$ , in which case the base would divide itself equally between the two acids, whereas, when we compare 4HCl with  $2\text{H}_2\text{SO}_4$ , the base would divide itself in the proportion of two equivalents to the former and one to the latter.

Now these theoretical deductions are entirely supported by the ascertained facts of the case.  $\text{HNO}_3$ , HCl, HBr, and HI, acids of which the heat of neutralisation is the same, and which form stable salts, divide the base between them equally, the relative numbers obtained by Thomsen being 100, 100, 89, and 79, and these numbers are certainly as nearly equal as could be expected, seeing that Thomsen's method contains many obvious sources of inaccuracy, for he regards certain small quantities as being negligible, he assumes certain actions to be represented by true hyperbolæ, which (judging from my results on the heat of dilution) they are not, and the water which he

used was only  $100\text{H}_2\text{O}$  per each equivalent, a quantity far too small to admit of the thermal results of dissolution being complete.\*

With  $\frac{1}{2}\text{H}_2\text{SO}_4$  and  $\frac{1}{2}\text{H}_2\text{SO}_4$ , in accordance with my deductions, we find that one-third only of the base is taken, the numbers found being 49 and 45 respectively,† while with the other acids investigated the numbers were as follows:—

Trichloroacetic acid.....	36
Orthophosphoric acid .....	25
$\frac{1}{2}$ Oxalic acid .....	24
Monochloroacetic acid.....	9
Hydrofluoric acid .....	5
$\frac{1}{2}$ Tartaric acid .....	5
$\frac{1}{3}$ Citric acid .....	5
Acetic acid .....	3
$\frac{1}{2}$ Boracic acid ( $\text{B}_2\text{O}_3$ ) .....	1
$\frac{1}{2}$ Silicic acid .....	0
Hydrocyanic acid .....	0

Of these, all except phosphoric and oxalic acid form salts dissociated by water,‡ and hence, in accordance again with my deductions, we find that they take either none of the base or but a small proportion of it; the dissociation of the trichloroacetates is very small comparatively, and hence the acid gives an exceptionally high value. With oxalic acid, the quadrantoxalate is probably formed, and hence  $2\text{C}_2\text{H}_2\text{O}_4$  instead of  $\frac{1}{2}\text{C}_2\text{H}_2\text{O}_4$  should be compared with  $\text{HNO}_3$ , in which case the value for the avidity would be 96, that is, nearly 100, as with other strong acids. With phosphoric acid only, the results seem rather anomalous, but it must be remembered that, in addition to other sources of uncertainty, these numbers were not obtained by direct comparison with nitric acid, but with sulphuric acid, where the results may be complicated by the formation of acid and double salts.

Ostwald (*J. pr. Chem.* [2], 19, 473) made some determinations of the so-called "avidity" of acids when used in normal and decinormal solutions, which showed that with the weaker acids the avidity was

\* For objections raised on other grounds see Hagemann, *Einige kritische Bemerkungen zur Aviditätsformell.* Berlin, 1887.

† *I.e.*, when  $\text{HNO}_3$  and  $\frac{1}{2}\text{H}_2\text{SO}_4$  is mixed with  $x\text{NaOH}$ , for every  $100\text{NaOH}$  taken by the former acid, the latter takes only 49, or one-third of the whole.

‡ The fluorides are certainly dissociated in solution, as is shown by their alkaline reaction and their action on glass. The abnormally large heat of neutralisation of hydrofluoric acid is probably due to the same causes as those which I have suggested (*Trans.*, 1885, 598) to meet the case of sulphuric acid: this would involve the recognition of the acid having a more complicated constitution than  $\text{HF}$  many facts, including its thermal reactions, render this very probable.

far greater when dilute than when strong. These results, apparently in opposition to my deductions above, are easily explained. The comparison was made by determining their relative action on calcium oxalate, and the more the calcium salt formed was dissociated, the more acid would there be left to continue the action on the oxalate. Directly opposite results would certainly be obtained by other methods.

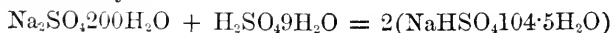
We assumed in the above that the heat of neutralisation of sulphuric acid was the same per H atom displaced as that of the other acids, namely, 13,800 cal. As a matter of fact, the experimental value is  $2 \times 15,690$  cal.\* for the displacement of the two atoms of hydrogen; but, as we have seen, in this case the two atoms of hydrogen are not displaced, but only the first one, and the displacement of this evolves only 14,754; but even this number is greater than it should be under perfect conditions, for, on the one hand, it would be reduced by several hundred cal. if the dilution were infinite, while, on the other, the acid salt formed is partially decomposed into the normal salt and free acid, a decomposition which evolves heat, and the removal of these two sources of evolution of heat would no doubt reduce the heat of neutralisation to the normal 13,800 cal.

One more difficulty which lies at the root of the matter remains to be explained, namely, why is the acid sulphate formed in preference to the normal sulphate, since the formation of the latter corresponds to the greater evolution of heat? Or, in other words, why does the normal salt combine with free acid to produce the acid sulphate with absorption of heat?

The explanation given by Berthelot (II, 642) is not, I believe, far from the truth. He points out that, although the reaction between the sulphate and acid in weak solutions is endothermic, yet between the anhydrous substances it would be accompanied by an evolution of heat. But it is not necessary to go back so far as the anhydrous substances to find an exothermic reaction, and, as these anhydrous substances do not exist in the solutions, by so doing we do not, in my opinion, obtain any real explanation. The reaction, however, will be exothermic when it takes place between the sulphate and any of the lower hydrates of the acid, some molecules of which must certainly be present, owing to dissociation, even in comparatively dilute solutions. Thus, although the reaction—



gives  $-1870$  cal., yet



\* The number refers to  $\text{H}_2\text{SO}_4 \cdot 200\text{H}_2\text{O}$ , with  $400\text{H}_2\text{O}$  it would be about 300 cal. smaller.



gives  $(-1870 + 2150 - 150 =) +130$  cal., and with still lower hydrates of the acid and of the normal sulphate, the reaction would become rapidly more exothermic. This reaction, being known to occur when the substances are taken in this degree of hydration, would necessarily occur here, and the removal of these lower hydrates of sulphuric acid from the sphere of action would necessitate a fresh dissociation of the higher ones to supply their places; hence the absorption of heat observed. The action is but an illustration of the principles here enunciated,—a possible action must always take place if it develops heat, whatever absorption of heat its occurrence subsequently involves, owing to the partial dissociation of the reagents.

It is scarcely necessary, however, to point out that this reaction is never complete, at any rate in weak solutions, for it is limited by the reverse action, the acid sulphate formed being dissociated back into free acid and neutral salt by the action of excess of water.\* And an increase in the amount of water present will not only increase this reverse action, but will also diminish the chances of the combination of the acid and normal salt by diminishing the proportion of the lower hydrates of the former in the liquid.

It will thus be seen that the whole notion of the distribution of a base between two acids being determined by certain constants peculiar to the acids termed their “affinity,” or “avidity,” becomes unnecessary and incorrect. And the manner in which this distribution occurs, instead of being irreconcilable with the results of the heat of neutralisation, as L. Meyer maintains, is determined solely by it, and the known laws of dissociation.

It is indeed incomprehensible how these ideas of “avidity” could have been accepted almost without question, as has been the case, unless it be that the interesting mathematical exercise relating to affinity, indulged in by Guldberg and Waage (*Études sur les affinités Chimique*, Christiania, 1867), was sufficient (as is generally the case when  $x$  and  $y$  is introduced into chemistry) to ensure the blind acceptance of that which common sense would reject.

What can be the meaning of an acid having a property which is a “constant,” and which yet varies continuously with a variation in the proportion of the solvent present.

In every case which has been investigated, the water has a most marked influence on the division of the base. Thus, Thomsen's results (I, 131), which he interpreted as showing that the water has no influence on the avidity, give—

\* This reaction would be exothermic with any hydrate of the acid sulphate which contains sufficient water to form on dissociation a hydrate of the acid higher than about  $\text{H}_2\text{SO}_4, 9\text{H}_2\text{O}$ .

Avidity of $\text{H}_2\text{SO}_4$ , when 150 $\text{H}_2\text{O}$ for each double equivalent is present .....	= 46
When 200 $\text{H}_2\text{O}$ is present.....	= 49
„ 300 „ .....	= 52*

while Berthelot, who combats the idea of this "avidity," gives the following values for the reaction of—

$\frac{1}{2}\text{K}_2\text{SO}_4$ on $\text{HNO}_3$ in total of 2 litres of water	—1810 cal.
„ „ „ 4 „	—1780 „
„ „ „ 8 „	—1600 „
„ „ „ 20 „	—1500 „

And Ostwald (*loc. sup. cit.*) gives, amongst others, the following numbers:—

Relative avidity of	In N solution.	In N/10 solution.
Formic acid .....	2.33	12.9
Acetic acid.....	1.05	7.35
Monochloroacetic acid .....	4.6	21.3
Citric acid.....	2.75	14.4

Yet these numbers have been accepted as being constants in each case.†

It must even be doubted whether the concordance between the values obtained by different methods is sufficient to warrant us in concluding that the numbers obtained really represent the division of the base which has taken place in the particular solutions investigated; thus the values for—

Sulphuric acid vary between nearly	100.0 and 46.0
Formic acid vary between.....	12.9 „ 2.6
Acetic acid vary between .....	7.4 „ 1.2
Monochloroacetic acid vary between ..	22.0 „ 5.1
Trichloroacetic acid vary between ....	89.9 „ 36.0
Oxalic acid vary between .....	43.0 „ 22.6
Isobutyric acid vary between .....	5.8 „ 0.9
Citric acid vary between .....	14.4 „ 3.1
and so on;	

numbers which no one who was not bent on proving a pet theory,

\* If the proportion of water was sufficient to dissociate all the acid sulphate formed, the  $\frac{1}{2}\text{H}_2\text{SO}_4$  would either take all the base or exactly half of it, according as its heat of neutralisation (to form the normal salt) in this state of dilution still remained greater than that of the nitric acid, 13,800 cal., or, which is quite possible, was reduced so as to be equal to it.

† Perhaps I am somewhat unfair in my criticism of Ostwald's opinions: he certainly admits that the water present, as well as the temperature, influence the values for the affinity to a very great extent; but, on the other hand, the whole idea of the existence of such a thing as a constant of affinity is dependent on its non-variation.

irrespective of fact, would ever have regarded as being identical in the respective cases.\*

When a base (NaOH) is mixed with two acids (HCl and HBr), of which the heat of neutralisation is the same, the enormous number of molecules actually taken in any experiment is sufficient reason for practically equivalent amounts of the two salts (NaCl and NaBr) being formed, but it is not so apparent why these same salts should be formed in equivalent proportions, as we know they are, when we mix one of them with the other acid, NaCl with HBr, for instance, unless dissociation occurs to such an extent that the fundamental molecules themselves are broken up into their constituent atoms, which would then combine with the other atoms of opposite character according to the frequency of collision, that is, in equivalent proportions. This resolution into atoms cannot, I think, be maintained, but the necessity for it is obviated if more than two hydrates of each substance, saturated to different extents, be present. For the lower and less saturated hydrates of the one salt might react with the higher hydrates of the opposite acid so as to produce an evolution of heat, while the same would occur with the lower hydrates of the other salt acting on the first acid, and thus we should get ever-occurring opposite reactions, admitting of the known interchange of radicles and soon resulting in a condition of equilibrium.

From the principle that the sum of the kinetic and potential energy of any system is an unalterable quantity, and that affinity is energy, it follows that the heat evolved in any reaction is the difference between the total energy of the system before and after the reaction, and hence it seems at first sight that we should be able to calculate the total energy in any substance, and, consequently, the heat evolved in any reaction, from a knowledge of the heat necessary to raise the reagents and compound from the absolute zero to the temperature of the reaction. The principle of this method is indeed applicable with absolute certainty to the determination of the *difference* in the heat evolved in any reaction at two different known temperatures (Person's principle, the non-application of which would mean that energy could be created and destroyed, see Trans., 1887, 329), but it fails when we attempt to apply it to any determination of the actual amounts measured by extending our arguments as far as the absolute zero, for the following reasons.

\* The most reliable thermal method (though even this would not be absolutely certain) would be to make a series of determinations with acids neutralised to different extents previously with the base, and to plot out the results in a diagram and thus find the proportional neutralisation requisite to form solutions which on being mixed would develop no heat. Thomsen's results quoted above were deduced from some determinations of this kind made by him.

(1.) The heat capacity of substances at ordinary temperatures affords no clue as to what their heat capacity would be at such low temperatures, indeed we have good reason to suppose that great, and comparatively sudden, changes would be experienced in this heat capacity before the absolute zero were reached (see L. Meyer, 87).

(2.) Because we do not know where this absolute zero may be situated: the generally accepted temperature of  $-273^{\circ}$  is simply what the zero would be if a gas remained a gas, and contracted regularly when cooled to this point; both of which suppositions we know to be incorrect: in questions on thermodynamics  $-273^{\circ}$  gives correct results, simply because it is applied only to cases where perfect gases are in question, and its use is simply equivalent to the statement that gases expand  $\frac{1}{273}$  of the volume at  $0^{\circ}$  C. for each degree.\*

Person's attempt (*Ann. Chim. Phys.*, **21**, 295; **27**, 250) to find the absolute zero from other data treated in a precisely similar manner, led to discordant results. Assuming that ice and water could remain as such at the absolute zero, and that they had then the same heat capacity as at known temperatures, he found that the absolute zero should be  $-160^{\circ}$  instead of  $-273^{\circ}$ , and if he had applied his principle (as it should be applicable if true) to the case of water and steam, he would have found the still less acceptable result  $+850^{\circ}$  C.† for his absolute zero. It is useless to base any theory on the supposition of facts being otherwise than we know them to be.

(3.) Because it by no means follows that, at the absolute zero of temperature, potential energy of affinity as well as kinetic energy would be non-existent. Facts, indeed, favour the contrary view. Affinity can cease to exist as such, that is, become converted into heat, only by being saturated by the combination of the substances endowed with it. No such saturation can take place on cooling a perfect gas, since a perfect gas is a substance in which the fundamental molecules never come within the sphere of each others

\* The confirmation of  $-273^{\circ}$  by Joule's evolution of Carnot's function (*Scientific Papers*, ii, 290) is not independent, as it is based on the coefficient of expansion of gases. Raoul Pictet's (*Compt. rend.*, **88**, 855) calculation of the melting points of the elements based on  $-273^{\circ}$  being the absolute zero, gives more acceptable confirmation, but it depends on an hypothesis to start with, and the variation of the constant obtained between the somewhat wide limits of 4 and 5 would allow of considerable latitude in the zero point taken.

† The absolute zero is, according to Person's argument, the temperature at which the heat of fusion of ice is *nil*, and similarly it should be that at which the heat of volatilisation of water is also *nil*. It appears to me that this latter temperature must be identical with the critical temperature of the liquid in question, but to calculate it properly we should have to take the actual (unknown) heat capacities at these temperatures, and not those at other lower temperatures, as is the case above.

attraction (in proof of<sup>o</sup> which we find that, when perfect gases combine to form a perfectly gaseous compound, the heat of their combination at constant volume is the same at all temperatures): with solids, the constancy in the heat given out in cooling, at most 6.4 cal. per atom, shows that the greater part of this is in all probability due to the fall of temperature only, and that very little of it is due to combination; this leaves but the heat evolved in the passage of the substance from the perfectly gaseous to the solid condition, less that evolved by the mere fall of temperature, to account for the total affinity possessed by the perfect gas, and this would I think fall far short of the amount of affinity known to be possessed by many gases, for it could rarely if ever amount to 10,000 cal. per molecule.\* The heat of neutralisation gives us, again, much information on this point, for it shows that the affinity which serves to unite the similar molecules of a solvent with each other, and which could alone become saturated by a fall of temperature, is not the only free affinity possessed by the molecules, for it is independent of that affinity owing to which these molecules combine with those of a salt and effect its dissolution; in other words, there is other affinity besides that which could become satisfied by cooling the liquid.

For these reasons the so-called absolute zero can give us no aid in calculating the heat evolved in a chemical reaction, and we must be content to wait for the present till some other means of doing so be discovered.

#### IV.—*The Isomeric Sulphonic Acids of $\beta$ -Naphthylamine.*

By ARTHUR G. GREEN.

By the sulphonation of  $\beta$ -naphthylamine under different conditions, four isomeric monosulphonic acids have been obtained [ $\alpha$  (Badische),  $\beta$  (Brönner's),  $\gamma$  (Dahl's), and  $\delta$  (Bayer's)], but our knowledge concerning them is still very incomplete. It therefore seemed of interest to communicate a few results which I have obtained in their investigation.

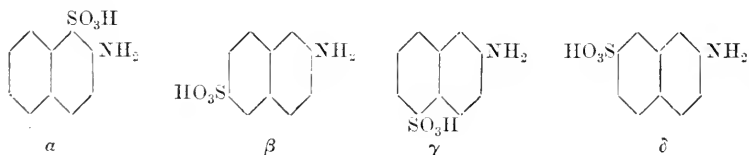
By heating  $\beta$ -naphthylamine with 3 to  $3\frac{1}{2}$  times its weight of ordinary sulphuric acid, at 100–105°, a mixture is obtained which

\* With  $\text{Br}_2$  it is, for instance, less than 8000 cal., and supposing it were as much as this with  $\text{H}_2$ , this would give the affinity of  $\text{H}_2 + \text{Br}_2$  as 16,000 only, whereas we know they combine to form  $2\text{HBr}$  with an evolution of 17,000 cal., and that this compound so formed is far from being saturated, as is shown by its heat of dissolution.

consists, according to Dahl (Germ. Pat., No. 29084, 32271, 32276), of the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -acids in the proportion of about 50 per cent. of  $\alpha$ , 10 per cent. of  $\beta$ , and 40 per cent. of  $\gamma$ . These can be separated by means of the difference in the solubilities of the sodium salts in spirit and of the barium salts in water. The proportion of the several isomerides varies greatly with the temperature at which the reaction takes place; thus by heating the above melt for some time at  $120^\circ$ , the quantity of  $\alpha$ -acid is greatly diminished, whilst that of the  $\beta$ -acid is increased. On the other hand, by sulphonation with three parts of fuming sulphuric acid (20 per cent. anhydride) at  $70$ – $80^\circ$  for a short time, about 70 per cent. of the  $\gamma$ - and 30 per cent. of the  $\alpha$ -acid is formed, but scarcely any of the  $\beta$ -acid. A similar mixture is obtained (Dahl, Germ. Pat., No. 32276) by agitating  $\beta$ -naphthylamine sulphate with ordinary sulphuric acid for two or three days at a temperature of  $15$ – $20^\circ$ . By heating  $\beta$ -naphthylamine hydric sulphate at  $200$ – $210^\circ$ , a product is obtained which consists chiefly of the  $\beta$ -acid (Liebmann, *Monit. Sci.*, 1885, 1043). By heating  $\beta$ -naphthylamine sulphate (1 part) with 3 parts of ordinary sulphuric acid at  $160$ – $170^\circ$ , for one hour, a mixture of about equal quantities of the  $\beta$ - and  $\delta$ -acids is formed (Bayer and Duisberg, *Ber.*, 20, 1426; C. Schultz, *Ber.*, 20, 1358). The  $\delta$ -acid is also obtained from  $\alpha$ -naphthalenedisulphonic acid by heating it under pressure at  $250^\circ$  with aqueous sodium hydrate, and then with ammonium chloride (A. Weinberg, *Ber.*, 20, 2906, 3353).

The  $\beta$ -naphthylamine- $\beta$ -sulphonic acid is obtained from  $\beta$ -naphthol- $\beta$ -sulphonic acid (Schaeffer's acid) by heating with ammonia under pressure (Farbfabrik, vorm. Brömmel, Germ. Pat., No. 22547).

The constitution of these four acids is probably represented by the formulæ—



In these formulæ, it will be seen that the  $\alpha$ - and  $\gamma$ -acids contain the  $\text{HSO}_3$  group in an  $\alpha$ -position, whilst in the  $\beta$ - and  $\delta$ -acids the  $\text{HSO}_3$  group is in the  $\beta$ -position.

This explains the influence of temperature on the formation of the several acids, for, like the  $\alpha$ - and  $\beta$ -sulphonic acids of naphthalene, the acids with the  $\text{HSO}_3$  group in the  $\alpha$ -position (the  $\alpha$ - and  $\gamma$ -acids) are formed at low temperatures, whilst those with the  $\text{HSO}_3$  group in the  $\beta$ -position (the  $\beta$ - and  $\delta$ -acids) are formed at higher temperatures. Also, just as  $\alpha$ -naphthalenesulphonic acid is converted into  $\beta$ -naphthalenesulphonic acid by heating with  $\text{H}_2\text{SO}_4$  to a higher temperature,

so each of the  $\alpha$ -acids of  $\beta$ -naphthylamine (the  $\alpha$ - or  $\gamma$ -acid) is converted into a mixture of the two  $\beta$ -acids (the  $\beta$ - and  $\delta$ -acids) by the same treatment.

*Products of the Sulphonation of  $\beta$ -Naphthylamine at 100—105°.*

$\beta$ -Naphthylamine was heated for five or six hours with 3—3½ times its weight of ordinary concentrated sulphuric acid at a temperature of 100—105°; the melt was poured into water, and the precipitate washed, pressed, and dried. For the separation of the isomeric acids, the method given in Dahl and Co's. patent was employed, and found to serve very satisfactorily. The acids were converted into the sodium salts, and boiled for an hour with six or seven times their weight of 90 per cent. spirit. The insoluble residue, after pressing and a final extraction, is the pure sodium salt of the  $\alpha$ -acid. From the sodium salt, the pure  $\alpha$ -acid was obtained, well crystallised in the form of prismatic tables. For this purpose, it was dissolved in boiling water, some ammonia added, and then acetic acid just short of precipitation; on cooling, the acid crystallises out. Precipitation with acetic acid from an ammoniacal solution was found to be a very convenient way of obtaining all these isomeric acids in a well-crystallised form. From the alcoholic filtrate containing the  $\beta$ - and  $\gamma$ -acids the spirit was distilled off, the residue dissolved in water, and precipitated with hydrochloric acid. The precipitated sulphonic acids were neutralised with barium hydrate and left to crystallise. A sparingly soluble barium salt crystallised out, whilst the mother-liquor contained the easily soluble barium salt of the  $\gamma$ -acid. From this, the  $\gamma$ -acid was set free by hydrochloric acid and obtained pure in the form of small plates by precipitation with acetic acid.

The sparingly soluble barium salt was purified by recrystallisation from water. According to Dahl, it consists of the salt of the  $\beta$ -acid only, but my experiments prove that it is a mixture of about equal parts of the  $\beta$ - and  $\delta$ -acids. By repeated fractional crystallisations from hot water, the two acids were separated. The more soluble one was found to be identical in appearance, properties, and in its sodium and ammonium salts with the  $\delta$ -acid obtained by Bayer's method of sulphonating at 170°. The  $\delta$ -acid was also obtained from the sodium last which crystallised out on cooling the hot alcoholic solution of the mixed sodium salts (see above). This, according to Dahl, is the sodium salt of the  $\beta$ -acid, but from my experiments it appears to consist almost entirely of the salt of the  $\delta$ -acid. The presence of the  $\delta$ -acid as well as the  $\beta$ -acid amongst the products of the sulphonation at 100° might certainly be expected, since, as has already been mentioned, both the  $\alpha$ - and  $\gamma$ -acids, which are probably the primary

products, are converted into mixtures of  $\beta$ - and  $\delta$ -acids on further heating with sulphuric acid.

The proportion in which the four isomerides are formed at  $100^\circ$  may be roughly estimated as about 50 per cent. of  $\alpha$ , 40 per cent. of  $\gamma$ , 5 per cent. of  $\beta$ , and 5 per cent. of  $\delta$ .

*Properties of the four Isomeric Acids.*

In the formulæ given above, it will be seen that the  $\alpha$ -acid differs greatly from the  $\beta$ -,  $\gamma$ -, and  $\delta$ -acids in being a homonuclear compound, whilst the other three are heteronuclear. This is fully borne out in their properties. Thus the  $\alpha$ -acid is the only one whose sodium salt is insoluble in spirit. The azo-compounds also show characteristic differences. For instance, the scarlets obtained by combining the diazotised acids with  $\beta$ -naphthol are very similar in shade, and readily soluble in water, whether the  $\beta$ -,  $\gamma$ -, or  $\delta$ -acid is employed, but that from the  $\alpha$ -acid is almost insoluble. Again, by combining diazotised primuline or benzidine with either the  $\beta$ -,  $\gamma$ -, or  $\delta$ -acids, scarlets of almost the same shade are obtained, but the  $\alpha$ -acid gives an orange. By diazotising, and boiling with dilute sulphuric acid, the  $\alpha$ -acid was converted into the corresponding  $\alpha$ -sulphonic acid of  $\beta$ -naphthol (Bayer's), whose sodium salt was soluble in alcohol, and crystallised from it in silky plates, exceedingly soluble in water. It is to be observed that the naphthylaminesulphonic acid, insoluble in spirit, corresponds to the naphtholsulphonic acid soluble in spirit.

The ammonium salts of the four acids are very characteristic. The ammonium salt of the  $\alpha$ -acid forms very soluble, large, solid prisms; that of the  $\gamma$ -acid exceedingly soluble tables; the  $\delta$ -salt tolerably soluble, small plates; whilst the  $\beta$ -salt, which is the least soluble of all, crystallises in beautiful, large, thin plates, often 1 or 2 inches long, and having a violet fluorescence. The ammonium salt of the  $\beta$ -acid serves very conveniently for its identification, and separation from the  $\delta$ -acid. The sodium salt of the  $\beta$ -acid crystallises in flat needles, which when air-dried, contain  $2\text{H}_2\text{O}$  (as given by Försling, *Ber.*, 20, 77). The sodium salt of the  $\delta$ -acid crystallises in plates (according to Bayer, in needles). In regard to the crystalline forms of the free acids, it has already been mentioned that the  $\alpha$ -acid crystallises in large tables, the  $\gamma$ -acid in plates. The  $\delta$ -acid, from whatever source it was obtained, always formed very fine, voluminous needles (as stated by Bayer and others). When quite free from acid, it is tolerably soluble in water. Since the occurrence of the  $\delta$ -acid together with the  $\beta$ -acid (whether obtained by sulphonation at  $100^\circ$  or from the sulphonic acid of  $\beta$ -naphthol) has hitherto not been suspected, it appears probable that the  $\beta$ -acid has scarcely ever been obtained quite pure. That this is indeed the case

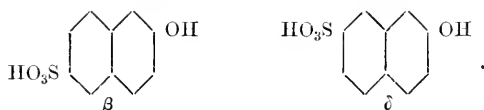


seems to be shown by the fact that the  $\beta$ -acid is always described as crystallising in lustrous plates (which are even regarded as very characteristic), whereas I found that when obtained from the pure ammonium salt it invariably crystallises in compact prismatic needles. In order to prove that this difference of crystalline form is due to a trace of  $\delta$ -acid, a small quantity of  $\delta$ -acid was added to an alkaline solution of pure  $\beta$ -acid (needles): on precipitating from the hot solution with an acid, the whole then came out in silky plates.

*$\beta$ -Naphthylaminesulphonic Acids from  $\beta$ -Naphtholsulphonic Acids.*

It is usually considered that two monosulphonic acids only are formed by sulphonating  $\beta$ -naphthol under varying conditions, viz., Bayer's acid and Schäffer's acid; the former being the chief product at a low temperature, the latter at a high temperature. Considering the analogous reactions of hydroxy- and amido-compounds, it seemed to me probable that, corresponding to the behaviour of  $\beta$ -naphthylamine,  $\beta$ -naphthol should give on sulphonation at a low temperature, a mixture of two  $\alpha$ -sulphonic acids ( $\alpha$  and  $\gamma$ ) which, by heating to a higher temperature, would be converted into two  $\beta$ -sulphonic acids ( $\beta$  and  $\delta$ ). The different behaviour of Schäffer's acid, so called when obtained under different conditions, strengthened this assumption, and led me to attempt to prove the presence of another acid associated with the  $\beta$ -acid. The product taken for investigation was the  $\beta$ -naphtholsulphonic acid, obtained according to Armstrong's method, by heating molecular proportions of  $\beta$ -naphthol and 100 per cent. sulphuric acid at  $100^\circ$ . The sulphonic acid so obtained is usually assumed to be identical with Schäffer's acid. As the separation of the  $\beta$ -naphtholsulphonic acids is very difficult, whereas that of the  $\beta$ -naphthylaminesulphonic acids is comparatively easy, the method which was employed consisted in converting the naphtholsulphonic acids into naphthylaminesulphonic acids by treatment with ammonia, and separating these. 100 grams of  $\beta$ -naphthol was heated with 70 grams of 100 per cent.  $\text{H}_2\text{SO}_4$  for 2 or 3 hours at  $100$ – $105^\circ$  till the reaction was complete, when the melt solidified to a hard mass of the sulphonic acids. This was dissolved in water, neutralised with sodium carbonate (filtering from a little tar which remains insoluble) and the sodium salt precipitated with sodium chloride. Or else the hot solution was neutralised with ammonia, when the sparingly soluble salt crystallised out on cooling. The yield of the ammonium salt is about 110 grams. The conversion into  $\beta$ -naphthylaminesulphonic acid was performed by heating with aqueous ammonia under pressure at  $250$ – $280^\circ$ , or by passing dry gaseous ammonia over the dry sodium salt heated to about  $280$ – $290^\circ$ . The product was precipitated with

sulphuric acid and submitted to a careful series of fractional precipitations, and crystallisations of the ammonium salt. By this means pure  $\beta$ - and  $\delta$ -sulphonic acids were isolated from it, and had all the properties previously described. The  $\beta$ -acid crystallised in prismatic needles, its ammonium salt in large, thin plates, and its sodium salt in flat needles. The  $\delta$ -acid crystallised in very fine matted needles, its ammonium salt in small plates, and its sodium salt in small plates. It is thus proved that the  $\beta$ -naphtholsulphonic acid, obtained by Armstrong's method, is a mixture of the  $\beta$ - and  $\delta$ -sulphonic acids, whose constitution is probably represented by the formulæ—



Whether the  $\gamma$ -acid occurs along with the  $\alpha$ -acid amongst the products of the sulphonation of  $\beta$ -naphthol at a low temperature, I have not yet been able to determine, but hope to be able to do so before long.

In conclusion, I desire to express my thanks to Messrs. Brooke, Simpson, and Spiller, in whose laboratory the above research was carried out.

#### V.—On Ethylic Cinnamyldiethacetate.

By F. E. MATTHEWS, Ph.D.

SOME time since I showed (*Chem. Soc. Trans.*, 1883, 200) that a condensation product of ethylic diethacetoacetate with benzaldehyde could be obtained by the action of hydrochloric acid gas upon the mixture of the two substances. The product was proved to have the constitution  $\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{C}(\text{C}_2\text{H}_5)_2\cdot\text{COOC}_2\text{H}_5$ , or ethylic cinnamyldiethacetate, but on account of the very poor yield of substance obtained, and the difficulty of purification, I was unable to do more with it than make analyses and obtain a bromine addition product.

Since that time I have found a method by which the yield of the substance may be very considerably increased, and as at the same time it is much simpler and more convenient, I have been able to prepare the substance in much larger quantities. In the previous process, the mixture of substances after saturation with hydrogen chloride was allowed to stand for a few days; it was then poured into ice-water, the separated oil washed with sodic hydrate, dried with calcium chloride, and fractioned in a vacuum. After some time, the

portion boiling at 200—205° at a pressure of 3 mm. solidified. It was then recrystallised from light petroleum, and thus obtained pure.

I have since found that, if instead of allowing the mixture saturated with gaseous hydrochloric acid to stand for four days only, it was allowed to remain for about a month, and that during this period the mixture was two or three times more treated with hydrochloric acid gas at a temperature of 0°, after this time crystals began to form in the mixture, and continued growing till the whole became a solid mass, but containing a large amount of the mother-liquor.

The crystals were collected in a funnel fitted with a platinum cone, and by means of a filter-pump, the mother-liquor was removed as far as possible, the latter was then again saturated with hydrochloric acid, when in a few days a further crop of crystals was produced. This process was repeated until no more benzaldehyde remained in the mixture. The various crops of the crystals were first drained on porous plates, and then dried by pressure between filter-paper and exposure to warm air. They were found to be free from chlorine, and they all melted between 100° and 102°.

A portion was recrystallised from ether for analysis; after recrystallisation, it resembled in every way the ethylic cinnamyldiethacetate previously prepared; it melted at 101—102°, and gave the following result on combustion:—

- I. 0.2023 gram of the substance gave 0.5469 gram  $\text{CO}_2$  and 0.1477 gram  $\text{OH}_2$ .  
 II. 0.2027 gram of the substance gave 0.5504 gram  $\text{CO}_2$  and 0.1463 gram  $\text{OH}_2$ .

	Calculated for $\text{C}_{17}\text{H}_{22}\text{O}_3$ .	Found.	
		I.	II.
C .....	74.45	73.73	74.05
H .....	8.03	8.11	8.02

Analysis I was made with the crude substance, II upon a portion that had been recrystallised.

The substance is therefore even without recrystallisation almost pure ethylic cinnamyldiethacetate.

An attempt was made to saponify some of the substance with caustic potash, but although a reaction took place it was not found easy to isolate the products. A small quantity of a potash salt was, however, obtained, and this yielded an acid which from its melting point appeared to be cinnamic acid, but the quantity was insufficient for an analysis.

On substituting baryta for potash, saponification took place much more readily. Some of the substance was placed in a flask connected with a Liebig's condenser, an excess of baryta-water was added, and

the mixture raised to the boiling point. The ether melted under the solution and a gradual deposition of barium carbonate was noticed, at the same time an oil, somewhat resembling peppermint in odour, distilled over in small quantity; it was separated from the water by means of ether, the ethereal solution dried, the ether distilled off, and the residue allowed to stand for some time, when it partly solidified. The crystals were separated from the liquid, and were found to melt at  $100^{\circ}$ ; the oil on analysis gave figures approximating to those required by the original substance. The distillate appears therefore to consist chiefly of the original substance, probably mixed with a small percentage of cinnamyl diethylmethyl ketone.

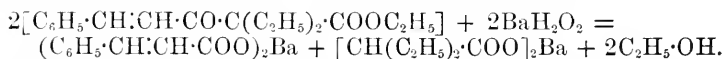
The residue in the flask after saponification was acidified with hydrochloric acid, when a dense white precipitate was produced which, after purification by dissolving in sodium carbonate, reprecipitating with hydrochloric acid, and subsequent crystallisation from dilute alcohol, melted at  $132-133^{\circ}$ , and possessed all the properties of cinnamic acid. It gave the following figures on analysis:—

0.1403 gram of the substance gave 0.3748 gram  $\text{CO}_2$  and 0.0740 gram  $\text{OH}_2$ .

	Theory for $\text{C}_9\text{H}_8\text{O}_2$ .	Found.
C .....	72.97	72.86
H .....	5.41	5.86

The diethacetic acid remaining in solution was not isolated.

The saponification of ethylic cinnamyl diethacetate by baric hydrate takes place chiefly according to the following equation:—



I have also tried to prepare the corresponding mon-ethyl compound in a similar manner, but after the mixture of ethylic ethacetoacetate and benzaldehyde saturated with hydrochloric acid had been standing for three months, no crystallisation was observable. This fact appears to confirm my previous observation that ethylic cinnamyl-monoethylacetate is not crystalline at ordinary temperatures.

The corresponding reactions with ethylic dimethyl- and mono-methyl-acetoacetates have also been investigated, but in every case I have failed in obtaining any definite product. The reaction appears to be much more complicated than that with the corresponding ethyl compounds, the complication being probably caused by the substituted methyl-groups in the substance also being capable of taking part in the condensation.

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VI.—*The Action of Ammonia on some Tungsten Compounds.*

By SAMUEL RIDEAL, D.Sc. Lond., Fellow of University College,  
London.

WÖHLER, in a paper "Ueber Amidverbindungen des Wolframs" (*Annalen*, **73**, 190), described the results of the action of ammonia on tungstic anhydride and tungsten chloride. In the former case, he found that when tungstic anhydride was heated to dull redness in a stream of dry ammonia, it was converted into a black compound, whilst water condensed in the cool part of the tube. The compound at a higher temperature yielded metallic tungsten. The analysis gave results which varied between the numbers 87.65 and 88.47 for the percentage of tungsten present, and a nitrogen determination gave 7.15 per cent. The compound also contained a small quantity of hydrogen, 0.2 per cent. From these data he concluded that the compound might be regarded as a mixture of nitride, amide, and oxide of tungsten, and he named the compound tungsten nitretamid-oxide. The formula with the modern atomic weight for tungsten is  $4\text{WN}_2, \text{W}_2(\text{NH}_2)_2, 2\text{WO}_2 = \text{W}_8\text{N}_{10}\text{H}_4\text{O}_4$ .

The action of ammonia on tungsten chloride, however, gave a nitrogen compound containing no oxygen. The percentage of tungsten in this varied between 86.76 and 90.80, and a determination of the percentage of nitrogen in the specimen containing the highest percentage of tungsten was found to be 8.24. From these results he concluded that two compounds were formed, represented by the formulæ  $2\text{WN}_2 + \text{W}(\text{NH}_2)_2$  (W, per cent. 86.58) and  $2\text{WN} + \text{W}(\text{NH}_2)_2$  (W, per cent. 90.44). The latter, it will be seen, is produced from the compound  $2\text{WN}_2, \text{W}(\text{NH}_2)_2$  by the removal of one molecule of nitrogen. It could also be obtained by heating the former compound in a current of hydrogen, when ammonia was formed. It is to be noted that the theoretical percentage of nitrogen in the latter compound should be 8.92, and that Wöhler obtained only 8.24 per cent. No determination of the amount of nitrogen or of hydrogen present in the former compound appears to have been made. In a later communication (*Annalen*, **105**, 258) he records the fact that when the chlorides of tungsten are heated with ammonium chloride similar black compounds are produced, which may be either the above-mentioned compounds or a nitride of the metal. No analyses of the compound prepared by this reaction are given.

It seemed of interest to compare these results with the action of

ammonia on the oxychlorides, and also to endeavour to obtain the compounds in a purer state.

Roscoe's work on the tungsten-derivatives has given to chemists a means of preparing the oxychlorides of tungsten, and the present note is to record the results which were obtained by substituting these for the hexachloride and also a re-examination of some of the compounds obtained by Wöhler.

*Action of Ammonia on Ignited Tungstic Anhydride.*

A current of dry ammonia was passed over a layer of tungstic anhydride heated to dull redness. Water condensed at the further end of the tube, and the pale yellow tungstic anhydride was converted into a black, amorphous product. After allowing the tube to cool, a current of dry air was drawn through it, to ensure the removal of any residual ammonia.

The compound was analysed by ignition in air, until the black colour was entirely destroyed and the weight became constant. The addition of a few drops of nitric acid helped the final oxidation of the tungsten, which was then strongly heated in order to destroy any compound with nitric acid which might be formed.

The results obtaining by noticing the decrease of weight in the tungstic anhydride after treatment with ammonia gave also a set of results which agreed with the determination of the percentage of tungsten obtained by the analysis of the compound. The mean of several experiments gave 85.26 for the percentage of tungsten in the compound, a determination of the nitrogen by Dumas' method showed that 0.3845 gram yielded 24.5 c.c. at 12.5° and 747 mm. = 7.4 per cent. N.

	Theory.	Found.
Tungsten.....	84.6	85.26
Nitrogen.....	7.6	7.4
Hydrogen .....	0.27	0.27
Oxygen.....	7.3	7.07

The formula with which these numbers best agree is  $W_5N_6H_3O_5$ , which indicates that the removal of the oxygen had not been so complete as in the experiments described by Wöhler.

*The Action of Ammonium Chloride on Tungstic Anhydride.*

When tungstic anhydride is mixed with ammonium chloride, and the mixture heated in a hard glass tube or small crucible, a black product is formed. After repeatedly reheating with fresh ammonium chloride the weight becomes constant. Different preparations, how-

ever, vary in the amount of tungsten they contain between the limits 83.9 and 81.0, the average of several experiments being 82.4 per cent. The amount of nitrogen in these products is much smaller than in the compound formed by the action of the ammonia. A compound containing 83.9 per cent. of tungsten having 6.7 per cent. of nitrogen, and that with 81.0 per cent. only 5.7 per cent. of nitrogen.

	Highest.	Lowest.	Mean.	Theory for $WN_2.WO_3$ .
Tungsten. . . .	83.9	81.0	82.4	82.8
Nitrogen. . . .	6.7	5.7	6.2	6.4

It will be noticed that an increase in the percentage of tungsten is accompanied by a rise in the amount of nitrogen, as if the tungstic anhydride,  $WO_3$  (W per cent. 79.3), was being converted into a nitride, say  $WN_2$ , whose percentage composition is  $W = 86.8$ ,  $N = 13.2$ .

*The Action of Ammonia on Tungsten Oxychloride,  $WO_2Cl_2$ .*

The oxychloride was prepared by Roscoe's method, and the ammonia, carefully dried, was passed into the tube in which the oxychloride was condensed, so as to prevent decomposition by contact with the moisture in the air. The reaction takes place without the application of heat, and white fumes of ammonium chloride are formed in the further part of the tube. The product, which is semicrystalline and of a dull, dark brown colour, was purified from ammonium chloride by gently heating the tube in a current of dry hydrogen. The analysis of several specimens prepared in this way yielded a percentage of tungsten varying between 84.5 and 85.6, with an average of 85.09. The product differed from the foregoing in not evolving ammonia on heating with soda-lime, and two determinations of the amount of nitrogen present only yielded a few cubic centimetres of gas. It seems, therefore, that, in this case, the ammonia removes chlorine from the molecule, and leaves the dioxide (W per cent. = 85.18) in a semicrystalline form. This result was partially confirmed by observing that a permanent gas was formed during the reaction.

It is interesting to note that the action of ammonia on this oxychloride of tungsten,  $WO_2Cl_2$ , is similar to that which I have previously shown to take place when dry ammonia is allowed to act upon chromyl dichloride,  $CrO_2Cl_2$  (Trans., 1886, 49, 367).

*Action of Ammonia on the Red Oxychloride,  $WOCl_4$ .*

This compound, which, on account of its unstable character, was only prepared in small quantity, is also rapidly attacked by dry

ammonia in the cold. A small quantity (0.2318 gram) of the black compound formed gave 0.2066 gram tungstic anhydride, from which it is seen that 88.9 per cent. of tungsten is present in the product. This was the highest percentage of tungsten in any of the products examined. The quantity formed did not permit of a nitrogen determination being made. If the remainder is chiefly nitrogen, it approaches in composition to a nitride of the formula  $W_2N_3$ , in which the percentage of tungsten is 89.5.

*The Action of Ammonia on Tungsten Hexachloride.*

Dry ammonia rapidly attacks the hexachloride in the cold, yielding white fumes of ammonium chloride and a black powder having a semi-metallic lustre. The latter can be freed from ammonium chloride by washing with water. It is insoluble in nitric acid, dilute sulphuric acid, and soda. When fused with soda, it gave off ammonia and was converted into sodium tungstate. It is oxidised by aqua regia to tungstic acid. Strong hot sulphuric acid converts it into ammonia and tungstic acid. When heated in the air it glows, and is converted into yellow tungstic anhydride. The oxidation to tungstic anhydride in the air was sometimes accompanied by a slight smell of ammonia, but when the substance had been well washed with water, or heated in a current of dry hydrogen until all the ammonium chloride had been volatilised, it did not give off ammonia when heated in this way. The percentage of tungsten, as determined by the ignition of the black compound to tungstic anhydride in the air, gave results varying between 87.3 and 92.8 per cent. The average of all the determinations gave 90.05 for the percentage of tungsten. It will be noticed that the lowest result obtained was slightly higher than the lowest determination by Wöhler. The decomposition of the compound by hot and strong sulphuric acid suggested Kjeldahl's method for estimating the nitrogen in this substance. Two determinations with different samples gave 10.57 for the amount of nitrogen present.

These results agree with those required by the formula  $W_2N_3$ .

	Found.	Calculated for $W_2N_3$ .
Tungsten.....	90.05	89.8
Nitrogen.....	10.57	10.2

The somewhat high result for the nitrogen constant may be due to the fact that the compound seems to have the property of condensing ammonia upon its surface. Wöhler determined the percentage of nitrogen in a specimen containing 90.8 per cent. of tungsten to be 8.24, and by assuming that hydrogen was also present arrived at the



formula  $2WN, W(NH_2)_2$ . The amount of tungsten in other specimens was less than this, the minimum obtained by him being 86.76. To account for this low result, he assumed that the difference was due to an increase in the nitrogen to 12.8 per cent., and that a second compound of the composition  $2WN_2, W(NH_2)_2$  was therefore produced when the conditions were slightly modified.

Finely divided metallic tungsten, after heating to redness in a current of dry hydrogen, underwent no alteration in weight when heated in a current of dry ammonia. No action was observed when dry ammonia gas was passed over the heated blue oxide. A black compound is produced when a solution of tungstic acid in aqueous ammonia is evaporated to dryness and the product gently heated in a covered crucible; water is given off, and the black crystalline product on heating in the air is converted into yellow crystalline tungstic anhydride. The acid salt is said to form the blue oxide on ignition in a closed vessel, but the compound does not appear to have been very carefully examined.

#### VII.—*The Action of Chromium Oxychloride on Pinene.*

By G. G. HENDERSON, B.Sc., M.A., Assistant to the Professor of Chemistry, University of Glasgow, and R. W. SMITH.

ÉTARD, in studying the action of chromium oxychloride as an oxidising agent (*Ann. Chem. Phys.* [5], **22**, 218), found that some of the terpenes yield compounds with this substance, which, when treated with water, give corresponding camphoaldehydes, but he merely mentions the fact, and gives no description of the camphoaldehydes obtained. It seemed to us of interest to examine these compounds more fully, and, for a commencement, we took pinene, the terpene boiling at 159–161°, which we obtained in a state of great purity.

Chromium oxychloride attacks pinene with almost explosive violence, and, therefore, in order to moderate the action, we employed 10 per cent. solutions of each substance in dry carbon bisulphide. The pinene solution was put into a flask connected with a reflux condenser, and kept cool by a stream of water, and the solution of chromium oxychloride was added in small portions by means of a dropping funnel. After each addition of the chromium oxychloride, a voluminous dark-brown precipitate was formed, and quickly settled to the bottom of the flask. When all of the reagent had been added,

the flask was allowed to remain for some time, until the precipitate had settled; the carbon bisulphide was then filtered off as rapidly as possible by aid of the pump, the precipitate washed with dry carbon bisulphide, dried at a gentle heat, and put into dry, well-stoppered bottles. The solid compound thus obtained is almost black when moist, but when dry it is of a light greyish-brown. When exposed to the air, it rapidly absorbs water and decomposes, and when heated to between  $80^{\circ}$  and  $90^{\circ}$  it loses 1 mol. of hydrogen chloride with slight explosion.

Analysis of the compound gave the following results:—

- I. 0.3710 gram substance gave 0.3594 gram carbon dioxide = 0.0980 gram carbon, and 0.1302 gram water = 0.0145 gram hydrogen.
- II. 0.530 gram substance gave 0.1780 gram  $\text{Cr}_2\text{O}_3$  = 0.1222 gram chromium.
- III. 0.485 gram substance gave 0.6128 gram silver chloride = 0.1516 gram chlorine.

			Found.		
			I.	II.	III.
Calculated for $\text{C}_{10}\text{H}_{16}, 2\text{CrO}_2\text{Cl}_2$ .					
$\text{C}_{10} \dots$	120	26.84 p. c.	26.42 p. c.	—	—
$\text{H}_{16} \dots$	16	3.58 „	3.90 „	—	—
$2\text{Cr} \dots$	105	23.49 „	—	23.05 p. c.	—
$2\text{O}_2 \dots$	64	14.32 „	—	—	—
$2\text{Cl}_2 \dots$	142	31.76 „	—	—	31.25 p. c.
<hr/>					
447 100.00					

Pinene, therefore, like the other substances investigated by Étard, forms with chromium oxychloride a solid compound which has the formula  $\text{C}_{10}\text{H}_{16}, 2\text{CrO}_2\text{Cl}_2$ . When thrown into cold water, this is immediately decomposed with evolution of a considerable amount of heat, and a heavy oil of a brown colour separates, while the chromium salts go into solution. This oil was extracted by shaking up the solution with ether, and the ethereal solution thoroughly washed, first with dilute caustic soda, and finally with water, dried with potassic carbonate, and the ether then distilled off. In this way a transparent brown oil was obtained, with a strong but pleasant aromatic odour. In order to purify it, a portion of it was first shaken with a saturated solution of sodium bisulphite, but no crystalline compound was formed. We then attempted to distil a part of it, but found that it was entirely decomposed by heat; heavy white fumes, with a suffocating and most disagreeable odour were given off, and a black resinous mass was left in the flask. Another portion of the oil was distilled with steam, and although a considerable residue of

resinous matter was left in the retort, a fair quantity of the oil was obtained, now apparently pure. (In preparing a second supply of the oil, after decomposing the solid chromium oxychloride compound with water, we did not extract with ether, &c., but simply passed sulphur dioxide through the solution in order to reduce any chromic acid that might be present, and then distilled off the oil with steam and dried it over potassic carbonate.) The oil was now golden-yellow in colour and perfectly transparent, with the same pleasant odour as it had before distillation with steam. Its sp. gr. at  $15^{\circ}$  is 1.01366.

Analysis of the oil gave the following results:—

- I. 0.1720 gram oil gave 0.4640 gram carbon dioxide = 0.1265 gram carbon, and 0.1602 gram water = 0.0178 gram hydrogen.
- II. 0.3075 gram oil gave 0.8298 gram carbon dioxide = 0.2263 gram carbon, and 0.2830 gram water = 0.0315 gram hydrogen.
- III. 0.2826 gram oil gave 0.0958 gram silver chloride = 0.0307 gram chlorine.

		Found.			
		Calculated for $C_{20}H_{33}OCl$ .	I.	II.	III.
$C_{20}$ ...	240	73.95 p. c.	73.51 p. c.	73.59 p. c.	—
$H_{33}$ ...	33	10.16 „	10.34 „	10.22 „	—
O ....	16	4.96 „	—	—	—
Cl....	35.5	10.93 „	—	—	10.86 p. c.
		<hr/> 424.5 100.00			

The simplest formula that can be given to the oil is, therefore,  $C_{20}H_{33}OCl$ . We were surprised to find chlorine in it, having expected to obtain an oxy-compound, possibly an aldehyde, and we therefore heated the oil for some time with alcoholic potash, but without altering its composition to any appreciable extent. Several analyses of the oil were made, both before and after distilling it with steam, but the results were in each case very close to those given above. It seems possible that the oil may be a mixture in equal proportions of  $C_{10}H_{15}O$  and  $C_{10}H_{15}Cl$ , but if this be so we were unable to separate it into two fractions. As stated above, it does not combine with sodic hydric sulphite. When heated with acetic chloride for some time, its colour becomes slightly darker, but it is otherwise unchanged, and it does not give any reaction either with hydroxylamine or phenylhydrazine; it does not alter on exposure to the air.

On attempting to distil the oil under ordinary atmospheric pressure, it is completely decomposed, but this is not the case when it is distilled under diminished pressure; the decomposition is then only partial. A small quantity of resinous matter is left in the flask, and an oil mixed with a little water comes over. The oil was dried, and again

distilled under diminished pressure, when it all came over between  $180^{\circ}$  and  $185^{\circ}$ . In appearance this oil is very similar to the one previously described; its odour is almost the same, and it behaves in the same way with alcoholic potash, sodium hydrogen sulphite, acetic chloride, and phenylhydrazine; its sp. gr., however, is rather less, being 0.97407 at  $15^{\circ}$ , and its composition is quite different, as is seen by the following analyses:—

- I. 0.2110 gram oil gave 0.6405 gram  $\text{CO}_2 = 0.1648$  gram C, and 0.1970 gram  $\text{H}_2\text{O} = 0.0219$  gram H.  
 II. 0.2525 gram oil gave 0.7225 gram  $\text{CO}_2 = 0.1970$  gram C, and 0.2340 gram  $\text{H}_2\text{O} = 0.0260$  gram H.  
 III. 0.3705 gram oil gave 0.1697 gram  $\text{AgCl} = 0.0420$  gram Cl.

		Found.			
		Calculated for $\text{C}_{20}\text{H}_{31}\text{Cl}$ .			
		I. II. III.			
$\text{C}_{20} \dots$	240.0	78.33 p. c.	78.13 p. c.	78.04 p. c.	—
$\text{H}_{31} \dots$	31.0	10.11 „	10.37 „	10.29 „	—
$\text{Cl} \dots$	35.5	11.56 „	—	—	11.34 p. c.
		306.5	100.00		

The simplest formula of this second oil is therefore  $\text{C}_{20}\text{H}_{31}\text{Cl}$ , and it is formed from the first on distillation by loss of 1 mol.  $\text{H}_2\text{O}$ .



This oil may also be a mixture of  $\text{C}_{10}\text{H}_{16}$  and  $\text{C}_{10}\text{H}_{15}\text{Cl}$  in equal proportions, but we again failed to split it up into any fractions.

We intend to prepare larger quantities of these oils, in order to examine them more closely, the results of our work being so different from what we expected.

#### VIII.—On Thionyl Thiocyanate.

By G. C. McMURTRY, Student in the Normal Schools of Science, South Kensington.

THIONYL CHLORIDE acts with great violence on mercuric thiocyanate. When the two substances are brought together the rise of temperature is sufficient to bring about the total decomposition of the mercuric salt. By mixing the thionyl chloride with carbon bisulphide, the reaction becomes more manageable, and results in the formation of

*thionyl thiocyanate* and mercuric chloride. Lead and silver thiocyanates are similarly acted upon by thionyl chloride, although with much less violence.

The best method of preparing the new compound is to allow the mixture of thionyl chloride and carbon bisulphide to act on excess of mercuric thiocyanate in a closed flask at the ordinary temperature. After standing for a few days, the liquid is decanted from the partially altered mercury salt, and allowed to evaporate in a vacuum. On washing the residue with hot benzene, and afterwards with ether, thionyl thiocyanate is left as an orange-coloured, amorphous powder.

It was analysed with the following results:—

- I. 0.2394 gram treated by Carius's method yielded 1.0154 gram barium sulphate.
- II. 0.0958 gram mixed with copper oxide and heated in a vacuum gave 22.32 c.c. nitrogen at 481 mm. pressure, and at 16.5° C. No nitric oxide was present.
- III. 0.2002 gram heated with copper oxide and lead chromate gave 0.1110 carbon dioxide.

These results are in sufficiently close accordance with the numbers demanded by the formula  $\text{SO}(\text{SCN})_2$ .

	Found.	Calculated.
S .....	58.26	58.53
N .....	17.46	17.07
C .....	15.11	14.63

Thionyl thiocyanate is an extremely stable substance. It is practically insoluble in cold water, and but slightly soluble in hot water. Hydrochloric acid even on boiling has no action on it; sulphuric acid in the cold does not attack it; it is, however, completely decomposed by hot oil of vitriol, with the evolution of sulphur dioxide and the precipitation of sulphur. It is but slightly soluble in ammonia; it is dissolved by hot benzene and by carbon bisulphide, but is quite insoluble in alcohol, ether, petroleum, phenol, chloroform, amyl alcohol, and acetic acid.

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IX.—On *Mercuric Chlorothiocyante*.

By G. C. McMURTRY, Student in the Normal Schools of Science,  
South Kensington.

ON treating the residue of mercurial salts obtained by the action of thionyl chloride on mercuric thiocyanate (see preceding paper) with hot water, the clear solution deposited crystals of a compound which analysis showed to be *mercuric chlorothiocyante*. This salt, which does not appear to have been previously prepared, may be readily obtained by treating a mixture of 5 parts of mercuric thiocyanate and 7 parts of mercuric chloride with boiling water, and allowing the clear solution to stand. The substance was analysed with the following results:—

- I. 0·4066 gram dissolved in dilute alcohol, mixed with hydrochloric acid, and treated with sulphuretted hydrogen, gave 0·3209 gram mercuric sulphide.
- II. 0·3786 gram heated with copper oxide in a vacuum gave 22·32 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 14·5° and 534 mm. pressure. After absorption of the nitric oxide there remained 22·32 c.c. of nitrogen at 14·5° and 485 mm. pressure.
- III. 0·2272 gram heated with copper oxide and lead chromate gave 0·0332 gram carbon dioxide.
- IV. 0·3731 gram treated by Carius's method gave 0·3010 gram barium sulphate.

These numbers lead to results which accord with the formula  $\text{Hg} < \begin{smallmatrix} \text{Cl} \\ \text{CS} \end{smallmatrix}$  or  $\text{HgCl}_2 \cdot \text{Hg}(\text{CSN})_2$ .

	Found.	Calculated.
Mercury.....	67·99	68·12
Nitrogen.....	4·71	4·77
Carbon.....	4·46	4·09
Sulphur.....	11·08	10·90

Mercuric chlorothiocyante is only sparingly soluble in cold water, but readily in hot water and in alcohol; it is also slightly soluble in ether. When heated on platinum foil, it intumesces in much the same way as mercuric thiocyanate. Its crystalline characters were kindly examined by Mr. Miers, who reports as follows:—

“Slender prisms having a prism angle of  $71\frac{1}{4}^\circ$ ; one fairly perfect cleavage (*c*) equally inclined to two prism faces which form the acute edge of the prism, and at an angle of  $42\frac{1}{4}^\circ$  to that edge; an imperfect

cleavage ( $\gamma$ ) equally inclined to the same two prism faces, and inclined at a smaller angle to that edge in the opposite direction.

System probably monosymmetric.

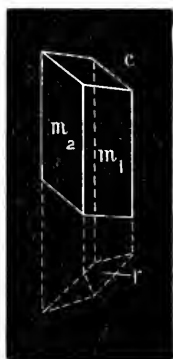
$$m_1 m_2 = 71^\circ 10'.$$

$$cm_1 = 64^\circ 30'.$$

If  $c$  is the basal plane,  $0P = (001)$ ,

and  $m$  is the prism  $00P = (110)$ .

Then  $a : b = 2.076 : 1$ .



“One optic axis is visible through a cleavage plate, and is not very far from perpendicular to  $c$ . A cross section at right angles to the prism shows only one axis. Plane of the optic axes is parallel to the plane of symmetry  $(010)$ .”

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X.—*Some Derivatives and New Colouring Matters obtained from  $\alpha$ -Pyrocresole.*

By WILLIAM BOTT, Ph.D., Berkeley Fellow of Owens College, and  
J. BRUCE MILLER, A.I.C., Owens College.

THE authors have been investigating the reactions of  $\alpha$ -pyrocresole and its derivatives, with a view of definitely ascertaining its constitution, and expect shortly to be able to publish their results. In the meantime it seemed worth while to describe a number of new derivatives which have been obtained, and whose preparation is not directly connected with the main research, as yet uncompleted.

*Trichlor- $\alpha$ -Pyrocresole*,  $C_{15}H_{11}Cl_3O$ .

This compound was obtained by the protracted action of chlorine on solutions of  $\alpha$ -pyrocresole in chloroform or carbon tetrachloride, and repeatedly recrystallising the product from boiling benzene. It forms a white, bulky mass consisting of slender, silky needles, which under the microscope are resolved into characteristic aggregates of thin, transparent, flat prisms or bars. The compound is insoluble in water, alcohol, ether, and acetic acid, but soluble in chloroform, and still more so in boiling benzene. Its melting point is very high, but cannot be determined with precision, as the substance, although quite pure, melts only gradually, first showing signs of melting about  $225^\circ$ . The following numbers were obtained on analysis:—

*Combustion.*

- I. 0.198 gram substance gave 0.418 gram  $CO_2$  and 0.0625 gram  $H_2O$ .  
 II. 0.268 gram substance gave 0.561 gram  $CO_2$  and 0.0775 gram  $H_2O$ .

*Chlorine Determination.*

- I. 0.1995 gram substance gave 0.2796 gram  $AgCl$ .

	Calculated for $C_{15}H_{11}Cl_3O$ .	Found.	
		I.	II.
C .....	57.41 p. c.	57.30	57.83 p. c.
H .....	3.50 „	3.43	3.21 „
Cl .....	33.98 „	34.62	— „
O (by difference).	5.11 „	5.11	5.11 „

It will be seen that in both analyses the carbon found is too high and the hydrogen too low, this discrepancy being accounted for by traces of chlorine, that is of hydrogen chloride, having found their way into the potash bulbs during combustion. The chlorine in the substance cannot be readily determined by Carius' method, as the compound is not always completely decomposed by nitric acid; the chlorine, therefore, was estimated by heating with pure lime.

*Dinitro- $\alpha$ -Pyrocresole Oxide*,  $C_{15}H_{10}(NO_2)_2O_2$ .

In a former paper, the three tetranitro-derivatives of the pyrocresoles have been described, no other nitro-compounds being known. We have lately obtained the first intermediate nitro-derivative, namely, dinitro- $\alpha$ -pyrocresole oxide, and are now trying to obtain the corresponding compounds from  $\beta$ - and  $\gamma$ -pyrocresole. The  $\alpha$ -derivative



was prepared by adding  $\alpha$ -pyrocresole oxide to cold, concentrated nitric acid, in small portions at a time, until a dark, reddish-brown solution was obtained. Upon the addition of water, a yellowish precipitate was thrown down consisting of a mixture of the dinitro-product with unaltered oxide. The latter was removed by extraction with boiling alcohol, and the residue recrystallised from glacial acetic acid or nitrobenzene. The pure substance forms yellowish-white crystals, which are very slightly soluble in hot water, slightly soluble in alcohol, a little more so in glacial acetic acid, and freely in hot nitrobenzene. They melt at about  $235^\circ$  with very slight decomposition, and when heated more strongly decompose, but do not burn with a flash like the tetra-nitro-compound. On analysis the compound gave the following numbers:—

0.192 gram substance gave 0.4075 gram  $\text{CO}_2$  and 0.063 gram  $\text{H}_2\text{O}$ .  
 0.195        ,,                       ,,       15.6 c.c. moist N at  $15^\circ$  and 748.5 mm.

	Calculated for $\text{C}_{15}\text{H}_{10}(\text{NO}_2)_2\text{O}_2$	Found.
C .....	57.32 p. c.	57.88 p. c.
H .....	3.18   ,,	3.64   ,,
O .....	30.57   ,,	(calc.) 30.57   ,,
N .....	8.92   ,,	9.22   ,,

#### *Reduction of the Nitro-compounds.*

The formation of amido- and other reduction-products has already been observed by W. Bott a considerable time ago, but we have only recently begun a closer study of the action of alkaline and acid reducing agents on the nitro-derivatives of the pyrocresoles. The results so far obtained open out a wide field of investigation, and comprise the beginnings of a new series of colouring matters, which probably differ essentially in composition and structure from the azo-colours already known. The compounds of  $\alpha$ -pyrocresole only have thus far been examined.

#### *Tetramido- $\alpha$ -Pyrocresole Oxide, $\text{C}_{15}\text{H}_8(\text{NH}_2)_4\text{O}_2$ .*

This compound has been obtained by the reducing action of tin on the corresponding nitro-derivative suspended in a mixture of strong hydrochloric and glacial acetic acid. The reaction is hastened by working under pressure. The amido-derivative is also formed by means of zinc-dust and acetic acid, hydriodic acid, and similar reducing agents in acid solution, but tin answers the purpose best. After complete reduction, the brownish-yellow solution is evaporated to expel excess of acid, the tin removed by sulphuretted hydrogen, and

the filtrate made slightly alkaline with caustic soda or ammonia, which precipitates the amido-compound as a greenish-yellow mass. This is well washed with water, and may be further purified by redissolving it in dilute hydrochloric acid, passing sulphuretted hydrogen to remove traces of tin which obstinately adhere to it, and reprecipitating the base with alkalis. It is not necessary to recrystallise the compound from alcohol, in which, moreover, it is not readily soluble. Tetramido- $\alpha$ -pyrocresole oxide thus prepared forms a greenish-yellow powder, sparingly soluble in alcohol and ether, and almost insoluble in benzene. It is soluble in acids, and the solutions give a dark reddish-brown coloration with sodium hypochlorite. The melting point appears to lie considerably above  $300^{\circ}$ , but has not yet been accurately ascertained.

0.140 gram substance gave 23.5 c.c. moist N at  $12^{\circ}$ , and 756 mm. bar.

	Calculated for $C_{15}H_8(NH_2)_4O_2$ .	Found.
N.....	19.71 p. c.	19.55 p. c.

*Diamido- $\alpha$ -Pyrocresole Oxide,  $C_{15}H_{10}(NH_2)_2O_2$ .*

This substance is obtained from the new dinitro-compound in the same manner as the previous derivative. Its properties have not yet been closely examined, but in appearance and solubility it greatly resembles the tetramido-compound.

0.161 substance gave 16 c.c. moist N at  $16^{\circ}$  and 761 mm. bar.

	Calculated for $C_{15}H_{10}(NH_2)_2O_2$ .	Found.
N.....	11.02 p. c.	11.40 p. c.

*Azo-derivatives of  $\alpha$ -Pyrocresole Oxide.*

Both the tetra- and di-amido-derivatives of  $\alpha$ -pyrocresole oxide can be diazotised in dilute acid solutions in the ordinary manner. It will, in all probability, be impossible to isolate the diazo-salts from these solutions, on account of the unstable character peculiar to these substances, but from the examination of some more stable derivatives, their composition, that is the number of diazo-groups present, may, we hope, be deduced. The solutions of these diazo-salts react in the well-known manner with phenols, giving rise to the formation of oxyazo-compounds. This reaction takes place most readily with alkaline solutions of  $\beta$ -naphthol, and the compounds thus formed represent the first colouring matters obtained from pyrocresoles.

If a diazotised solution of tetramido- $\alpha$ -pyrocresole oxide is added

to an alkaline solution of  $\beta$ -naphthol, a bright-red precipitate is immediately thrown down, consisting of the oxyazo-compound. After washing with cold water, and drying on a water-bath, it forms a dark-red powder, insoluble in water, but soluble in alcohol, ether, chloroform, and benzene. With concentrated sulphuric acid, it gives a beautiful and characteristic reaction, dissolving in the strong acid with a dark-green colour, which on gradual dilution with water changes to red, the colouring matter being reprecipitated in red flakes. This reaction somewhat resembles the test given by safranine, which also dissolves in concentrated sulphuric acid with a green colour. With safranine, the green colour is, however, readily discharged by a drop of strong nitric acid, which in the case of the new colouring matter changes the colour from green to purple, but does not discharge it. By means of fuming acid containing 30 to 60 per cent. of  $\text{SO}_3$ , the colouring matter can be sulphonated and obtained in solution. It dyes silk and wool a fine maroon shade.

By the action of diazotised solutions of diamido- $\alpha$ -pyrocresole oxide on alkaline solutions of  $\beta$ -naphthol, a red colouring matter is formed resembling the previous compound in all respects, but possessing a brighter and finer shade. Like the preceding compound it gives a highly characteristic test with strong sulphuric acid, and yields soluble sulphonic acids suited for dyeing purposes. It imparts to silk and wool a bright salmon colour.

By the action of the diazo-salts on an alkaline solution of  $\alpha$ -naphthol, a brownish colouring matter is formed, which dissolves in strong sulphuric acid, with a beautiful dark-blue colour, and is reprecipitated by water. The closer examination of the above colours is being proceeded with, and we shall extend the reaction to other monophenols, and to the meta-series of the diphenols and amidophenols.

Regarding the composition of these new colouring matters, we can at present only conclude from their mode of formation that they are oxyazo-compounds or trapæolins, but the number of azo-groups contained in their molecules remains to be ascertained by a careful estimation of the nitrogen in the purified products. We shall then also be able to deduce the formulæ of the diazo-compounds originally present in solution.

The action of reducing agents in alkaline solution on the nitro-derivatives of  $\alpha$ -pyrocresole oxide gives rise to the formation of azo-compounds, and also of small quantities of amido-products. The reaction with ammonium sulphide is particularly interesting. If a small quantity of tetranitro- $\alpha$ -pyrocresole oxide is heated with alcohol and a few drops of ammonium sulphide, the supernatant liquid assumes a reddish-brown colour, and on the addition of hydrochloric acid and warming, a red precipitate is thrown down, insoluble in water

but soluble in chloroform, ether, benzene, and acetone, with a reddish-violet colour. It is practically insoluble in carbon bisulphide, and may thus be separated from any admixture of sulphur. It dissolves in concentrated sulphuric acid, yielding a yellow solution, and is re-precipitated by water in dark-red flakes. If in the above experiments the action of the ammonium sulphide is allowed to continue for some time, the solution with hydrochloric acid no longer yields a red colour; on diluting with water, a yellow precipitate is formed, soluble in alcohol, ether, and chloroform, but almost insoluble in benzene. It is very sparingly soluble in cold water, a little more so in hot water, the solution dyeing silk a bright-yellow shade.

As the red and yellow substances have only been prepared quite recently, we have not had time to study them more closely. From the manner in which they are produced it appears probable, however, that the red substance is an azoxy- or oxyazo-derivative, whilst the yellow substance is derived from it by reduction.

The probable constitution of the derivatives described in this communication will be discussed in our next paper on the structure of  $\alpha$ -pyrocresole.

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## XI.—*Some Metallic Derivatives of Halogen Nitrophenols.*

By ARTHUR R. LING.

HAVING, in my experiments with the nitrohalogen-derivatives of phenol, obtained some metallic salts which have not, so far as I am aware, been described, and which appear to be in themselves of some little interest, I have deemed it advisable to publish a description of the same. Although I do not claim to have obtained results of any theoretical importance, it must be granted that any addition to our knowledge of this most interesting class of compounds cannot be without some value.

### *Bromination of Orthochloroparanitrophenol.*

The orthochloroparanitrophenol obtained by chlorinating paranitrophenol in acetic acid solution, was separated from the small quantity of dichloroparanitrophenol formed at the same time by converting it into the barium salt and crystallising from water. On decomposing the aqueous solution of this salt,  $[\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)\cdot\text{O}]_2\text{Ba}\cdot 7\text{H}_2\text{O}$ , with dilute hydrochloric acid, and subsequent crystallisation of the colour-

less chloronitrophenol from a large bulk of hot water, it was obtained in long, white, satiny needles melting at  $110^{\circ}$ , as stated by other observers.

The pure compound was dissolved in glacial acetic acid, and treated with the theoretical quantity of bromine (1 mol.) in the usual way, after which the solution was poured into water, and the precipitated chlorobromo-derivative converted into the potassium salt, which crystallises from water in golden-yellow needles. On decomposing the latter with dilute hydrochloric acid and crystallising the resulting compound from boiling water (in which it is but sparingly soluble), it was obtained in colourless crystals, resembling in appearance dichloro- and dibromo-*para*-nitrophenol, and melting sharply with instantaneous decomposition at  $137^{\circ}$ . A specimen of the pure compound dried at  $100^{\circ}$  gave the following result on analysis:—

0.4497 gram gave 0.5890 gram AgCl, AgBr.

	Theory.	Found.
	$C_6H_2ClBr(NO_2) \cdot OH$ .	
Cl } .....	45.74 per cent.	45.72 per cent.
Br }		

*Potassium chlorobromoparanitrophenol* forms long, golden-yellow needles, which contain 1 mol.  $H_2O$ , and are moderately soluble in cold water, easily in hot. It is thus analogous in composition to potassium dichloroparanitrophenol (Kollrepp, *Annalen*, **234**, 8). Analysis of an air-dried specimen gave the following results:—

0.3639 gram lost 0.0211 gram at  $100$ — $120^{\circ}$ , and gave 0.1036 gram  $K_2SO_4$ .

	Theory.	Found.
	$C_6H_2ClBr(NO_2) \cdot OK, H_2O$ .	
$H_2O$ .....	5.83 per cent.	5.79 per cent.
K .....	12.64 „	12.74 „

*Calcium chlorobromoparanitrophenol* appears to resemble calcium dichloroparanitrophenol (Armstrong, this Journal, 1871, 1117); thus it crystallises in long, yellow, glistening needles containing 9 mols.  $H_2O$ , but the following difference is to be noted: the dichloro-derivative is completely dehydrated at  $160^{\circ}$ , whilst the chlorobromo-salt requires heating to  $210^{\circ}$ . On exposing the above to the air, the needles soon effloresce, and become somewhat darker in colour and dull in appearance. After, however, losing 2 mols.  $H_2O$ , the hydrate  $[C_6H_2ClBr(NO_2) \cdot O]_2Ca, 7H_2O$  appeared to remain perfectly constant. This efflorescence takes place so quickly that it was found advisable to make the analytical determinations as soon after the salt had been dried between filter-paper as possible.

- I. 0.2556 gram lost 0.0586 gram at  $210^{\circ}$  and gave 0.0488 gram  $\text{CaSO}_4$ .  
 II. 0.5099 gram lost 0.1190 gram at  $210^{\circ}$  and gave 0.0960 gram  $\text{CaSO}_4$ .

	Theory. [ $\text{C}_6\text{H}_2\text{ClBr}(\text{NO}_2)\cdot\text{O}$ ] $_2\text{Ca}, 9\text{H}_2\text{O}$ .	Found.	
		I.	II.
$\text{H}_2\text{O}$ . . . . .	22.98 p. e.	22.92 p. e.	23.33 p. e.
Ca . . . . .	5.67 „	5.59 „	5.53 „

It may be stated that in all cases in which duplicate determinations are given, they have been taken from different preparations. The effloresced salt gave the following numbers:—

- I. 0.2543 gram lost 0.0480 gram at  $210^{\circ}$  and gave 0.0506 gram  $\text{CaSO}_4$ .  
 II. 0.2983 gram gave 0.0592 gram  $\text{CaSO}_4$ .

	Theory. [ $\text{C}_6\text{H}_2\text{ClBr}(\text{NO}_2)\cdot\text{O}$ ] $_2\text{Ca}, 7\text{H}_2\text{O}$ .	Found.	
		I.	II.
$\text{H}_2\text{O}$ . . . . .	18.83 p. e.	18.87 p. e.	—
Ca . . . . .	5.97 „	5.85 „	5.83 p. e.

If, instead of allowing the supersaturated solution of the above salt in water to cool to the temperature of the room, it is kept at about  $70^{\circ}$ , the salt separates in an entirely different form, namely, in dark-yellow, rhombic plates, which appear to contain 4 mols.  $\text{H}_2\text{O}$ . The analytical results were as follows:—

- I. 0.2557 gram lost 0.0301 gram at  $210^{\circ}$ , and gave 0.0557  $\text{CaSO}_4$ .  
 II. 0.2763 gram gave 0.0606 gram  $\text{CaSO}_4$ .

	Theory. [ $\text{C}_6\text{H}_2\text{ClBr}(\text{NO}_2)\cdot\text{O}$ ] $_2\text{Ca}, 4\text{H}_2\text{O}$ .	Found.	
		I.	II.
$\text{H}_2\text{O}$ . . . . .	11.70 p. e.	11.77 p. e.	—
Ca . . . . .	6.50 „	6.41 „	6.44 p. e.

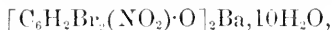
I am not aware that a calcium salt, analogous to the above, has yet been described.

*Barium chlorobromoparanitrophenol* forms long, canary-yellow glistening needles, and is similar in composition to barium dibromoparanitrophenol [ $\text{C}_6\text{H}_2\text{Br}_2(\text{NO}_2)\cdot\text{O}$ ] $_2\text{Ba}, 10\text{H}_2\text{O}$ , Brunck (*Zeit.*, 1867, 294). Analysis:—

- I. 0.2676 gram lost 0.0586 gram at  $200^{\circ}$ , and gave 0.0758 gram  $\text{BaSO}_4$ .  
 II. 0.3558 gram gave 0.1024 gram  $\text{BaSO}_4$ .

	Theory.	Found.	
		I.	II.
$[\text{C}_6\text{H}_2\text{ClBr}(\text{NO}_2)\cdot\text{O}]_2\text{Ba}, 10\text{H}_2\text{O}.$			
$\text{H}_2\text{O} \dots\dots\dots$	21.97 p. c.	21.90 p. c.	—
$\text{Ba} \dots\dots\dots$	16.70 „	16.62 „	16.91 p. c.

Brunck mentions (*loc. cit.*) that when the compound,



before alluded to, is placed over concentrated sulphuric acid in a desiccator, it dries up to a red powder, but it was afterwards shown by Post (*Annalen*, **205**, 94) that the form of the crystals remains unaltered, and that the change of colour from yellow to red is accompanied by the loss of  $6\frac{1}{2}$  mols.  $\text{H}_2\text{O}$ , the red needles having the composition  $[\text{C}_6\text{H}_2\text{Br}_2(\text{NO}_2)\cdot\text{O}]_2\text{Ba}, 3\frac{1}{2}\text{H}_2\text{O}$ . I may mention that I have described an analogous red barium salt of dichloroparanitrophenol (*Trans.*, 1887, 786). When the last-described yellow salt of chlorobromoparanitrophenol is allowed to remain over sulphuric acid for several hours, a precisely similar change takes place, for example,—

- I. 0.4754 gram yellow salt lost 0.0691 gram in 64 hours, and changed in colour to red.
- II. 0.6351 gram lost 0.0904 gram in 60 hours.

	Theory.	Found.	
		I.	II.
$[\text{C}_6\text{H}_2\text{ClBr}(\text{NO}_2)\cdot\text{O}]_2\text{Ba}, 3\frac{1}{2}\text{H}_2\text{O} + 6\frac{1}{2}\text{Aq}.$			
$\text{H}_2\text{O} \dots\dots\dots$	14.26 p. c.	14.53 p. c.	14.23 p. c.

The following numbers were also obtained on analysing the red salt:—

- I. 0.2331 gram lost 0.0214 gram at  $200^\circ$ , and gave 0.0765 gram  $\text{BaSO}_4$ .
- II. 0.2318 gram gave 0.0773 gram  $\text{BaSO}_4$ .

	Theory.	Found.	
		I.	II.
$[\text{C}_6\text{H}_2\text{ClBr}(\text{NO}_2)\cdot\text{O}]_2\text{Ba}, 3\frac{1}{2}\text{H}_2\text{O}.$			
$\text{H}_2\text{O} \dots\dots\dots$	8.96 p. c.	9.18 p. c.	—
$\text{Ba} \dots\dots\dots$	19.48 „	19.30 „	19.58 p. c.

A red salt, probably identical with the above, was deposited from supersaturated aqueous solutions of barium chlorobromoparanitrophenol, if the temperature was kept at about  $70^\circ$ ; but after the needles had been dried between filter-paper, they were, in every experiment tried, found to be partially converted into a yellow salt, and so were not further examined.

*Calcium Parachlorothobromorthonitrophenol.*

This salt has already been described by me (Trans., 1887, 789) as crystallising in orange-red glistening scales, containing  $2\frac{1}{2}$  mols.  $\text{H}_2\text{O}$ , but I find that my analytical numbers were wrongly calculated, and as another specimen, lately prepared, does not agree with the above description, I have re-examined the compound. It forms small glistening plates of a dark red colour, in fact, it is of quite as dark a colour as the isomeric compound containing  $7\text{H}_2\text{O}$  (*loc. cit.*, 791). It, however, becomes much lighter in colour on losing its water of crystallisation (orange when anhydrous), a fact which would seem to indicate that the specimen previously examined was partially dehydrated. It appears to be generally characteristic of these calcium salts that they retain some of their water of crystallisation at high temperatures. In the paper before referred to, it was shown that, in order to completely dehydrate calcium orthochloroparabromorthonitrophenol, it was necessary to heat it for a considerable time at  $250^\circ$ . When I first re-examined the salt under consideration, I concluded that it contained 3 mols.  $\text{H}_2\text{O}$ , as the following analysis seemed to indicate:—

0.2715 gram lost 0.0244 gram at  $100\text{--}125^\circ$ , and gave 0.0602 gram  $\text{CaSO}_4$ .

Theory.		Found.
$[\text{C}_6\text{H}_2\text{ClBr}(\text{NO}_2)\cdot\text{O}]_2\text{Ca}, 3\text{H}_2\text{O}$ .		
$\text{H}_2\text{O}$ .....	9.04 per cent.	8.98 per cent.
Ca.....	6.70 „	6.51 „

On heating another specimen, however, at  $200^\circ$ , till its weight remained constant, I found that a further loss occurred, and, confirmed as the result is, to a certain extent, by the halogen determination, there is little doubt that the salt in reality contains 4 mols.  $\text{H}_2\text{O}$ ; for example:—

I. 0.2911 gram lost 0.0338 gram at  $200^\circ$  and gave 0.0654 gram  $\text{CaSO}_4$ .

II. 0.3634 gram gave 0.3850 gram  $\text{AgCl}, \text{AgBr}$ .

Theory.		Found.	
$[\text{C}_6\text{H}_2\text{ClBr}(\text{NO}_2)\cdot\text{O}]_2\text{Ca}, 4\text{H}_2\text{O}$ .		I.	II.
$\text{H}_2\text{O}$ .....	11.70 p. c.	11.61 p. c.	—
Ca.....	6.50 „	6.49 „	—
Cl } .....	37.56 „	—	36.99 p. c.
Br }			



*Calcium Dichlororthonitrophenol.*

This is deposited from its hot aqueous solution in orange, fibrous needles, which are sparingly soluble in boiling water. Analysis:—

0.1537 gram dried at 100° gave 0.0443 gram  $\text{CaSO}_4$ .

Theory.		Found.
$[\text{C}_6\text{H}_2\text{Cl}_2(\text{NO}_2)\cdot\text{O}]_2\text{Ca}\cdot\text{H}_2\text{O}$		
Ca . . . . .	8.47 per cent.	8.45 per cent.

If a saturated solution of the above salt be left over sulphuric acid to evaporate slowly, it will be obtained in small dark-red needles and plates which probably contain 4 mols.  $\text{H}_2\text{O}$ . When heated at 135°, they were found to lose 19.67 per cent. of their weight, which agrees with the theory for 3 mols.  $\text{H}_2\text{O}$ ; the calcium determination is, however, nearer that demanded for  $4\text{H}_2\text{O}$ .

0.2566 gram gave 0.0664  $\text{CaSO}_4$ .

Theory.		Found.
$[\text{C}_6\text{H}_2\text{Cl}_2(\text{NO}_2)\cdot\text{O}]_2\text{Ca}\cdot 4\text{H}_2\text{O}$		
Ca . . . . .	7.60 per cent.	7.60 per cent.

This salt could not be further examined, as I had no more at my disposal.

*Calcium Dibromorthonitrophenol.*

This forms red scales containing  $7\text{H}_2\text{O}$ , and is analogous, therefore, to calcium orthochloroparabromorthonitrophenol. It is impossible to remove all the water of crystallisation from the above below the temperature at which it decomposes.

- I. 0.2352 gram gave 0.0423 gram  $\text{CaSO}_4$ .  
 II. 0.3065 „ 0.0541 „  $\text{CaSO}_4$ .  
 III. 0.2190 „ 0.2178 „  $\text{AgBr}$ .

Theory.		Found.		
$[\text{C}_6\text{H}_2\text{Br}_2(\text{NO}_2)\cdot\text{O}]_2\text{Ca}\cdot 7\text{H}_2\text{O}$		I.	II.	III.
Ca . . . .	5.28 p. c.	5.27 p. c.	5.18 p. c.	—
Br . . . .	42.21 „	—	—	42.41 p. c.

*Calcium Parabromorthiodorthonitrophenol.*

Parabromorthiodorthonitrophenol was first described by Körner (*Jahrb.*, 1867, 617), according to whom it melts at  $104.2^\circ$ , and next by Groth (*Jahrb.*, 1877, 549), who states that the crystals are brownish-yellow and melt at  $102^\circ$ ; he gives measurements of them.

This compound was prepared by me by iodising parabromortho-nitrophenol, m. p.  $88^{\circ}$ , in alcoholic solution with iodine and mercuric oxide. After purification by means of its potassium salt, and subsequent decomposition of the latter and crystallisation from alcohol, it was obtained in yellow scales of a somewhat dirty appearance melting at  $104^{\circ}$ . The calcium salt forms dark-red plates containing 4 mols.  $\text{H}_2\text{O}$ . Analysis:—

I. 0.2295 gram lost 0.0204 gram at  $190^{\circ}$  and gave 0.0397 gram  $\text{CaSO}_4$ .

II. 0.3441 gram gave 0.3652 gram  $\text{Ag}(\text{Br}, \text{I})$ .

	Theory. $[\text{C}_6\text{H}_2\text{BrI}(\text{NO}_2 \cdot \text{O})_2\text{Ca}, 4\text{H}_2\text{O}]$	Found.	
		I.	II.
$\text{H}_2\text{O}$ .....	9.03 p. c.	8.89 p. c.	—
$\text{Ca}$ .....	5.02 „	5.09 „	—
$\text{Br} \left. \begin{array}{l} \text{I} \end{array} \right\}$ .....	51.82 „	—	51.93 p. c.

Of the foregoing calcium salts of orthonitrophenol-derivatives, it is to be remarked that they all pass from a red to an orange colour with the loss of their water of crystallisation; this is at variance with the observations of Carnelley and Alexander, who state (*Proc.*, 1888, 64) that in the metallic derivatives of the nitrophenols the colour passes towards the red end of the spectrum as the water of crystallisation diminishes. It is also noteworthy that calcium dichlorortho-nitrophenol has less tendency to unite with water than the other calcium dihalogen orthonitrophenol-derivatives; for example, the monohydrate (an orange salt) is formed with ease, whilst the red salt containing 4 mols.  $\text{H}_2\text{O}$  is only obtained by slowly evaporating the solution over concentrated sulphuric acid.

As regards the colour of the salts of the nitrophenols, it is to be observed that those from the alkali metals, potassium and sodium, &c., of derivatives of orthonitrophenol are red, whilst those of para-nitrophenol are yellow; also that those of ortho-orthodinitrophenol and its derivatives are red, and those of orthoparadinitrophenol are yellow. In a paper by Nölting and Pick, published in a recent number of the *Berichte* (21, 3158—3160), two isomeric dinitroxylenols, from ortho-xylene, are described; one melting at  $127^{\circ}$ , having the  $\text{NO}_2$ -groups in the two ortho-positions with respect to the  $\text{OH}$ -group, and the other melting at  $82^{\circ}$ , and having the  $\text{NO}_2$ -groups in ortho-para-positions with respect to the same. Now, according to the authors, the salts of both these compounds are yellow, and thus it would seem that the introduction of two methyl-groups in the place of two hydrogen-atoms brings about a con-

siderable modification in the colour in the case of ortho-orthodinitrophenol, removing it further from the red end of the spectrum. Ortho-orthodinitrophenol and its halogen substitution-derivatives melt at a lower temperature than orthoparadinitrophenol and its corresponding derivatives; but this state of things seems to be reversed by the introduction of the two methyl-groups into the molecule, and the derivative of ortho-orthodinitrophenol then melts at the higher temperature.

## XII.—On Berberine. (Part I.)

By W. H. PERKIN, JUN., Ph.D.

BERBERINE, the yellow alkaloid of *Berberis vulgaris*, was discovered in the year 1826 by Chevallier and Pelletan (*Journ. de Chim. Médicale*, 2, 314) in *Xanthoxylum clava Herculis*, and described by them under the name of xanthopierit.

Subsequent researches have shown that this alkaloid is a constituent of a large number of plants, in some of which it is present in considerable quantities.

It has been found in *Cocculus palmatus*, or Columbo root (Boedecker, *Annalen*, 66, 384; 69, 40); in *Berberis vulgaris* (Buchner, *Ann.*, 24, 228); in *Caroline polycarpa* (Stenhouse, *Ann.*, 95, 108; 105, 360); in the wood of *Cosciniun fenestratum* from Ceylon, and in *Xanthorrhiza apii folia*, a North American plant of the Ranunculacea order (Perrins, *Ann.*, 83, 276); in *Hydrastis canadensis* (Mahla, *Sill. Am. J.* [2], 33, 43 (1862)); another North American plant of the Ranunculacea order, which, as it contains about 4 per cent. of crude alkaloid, and is readily obtainable in England, can be used as a source of the alkaloid (Perrins, *Ann.*, Suppl. 2, 173).

Berberine has also been found in *Woodumpar*, a yellow wood from Upper Assam, in the root of *Coptis tecta* or Mahmira—a plant growing in Hindoostan and China, and which is much valued in India on account of its tonic properties. Perrins (*loc. cit.*, p. 174), who examined this source, obtained as much as 8½ per cent. berberine from the root—a far larger quantity than has up to the present been found in any plant.

The French chemists Chevallier and Pelletan, the discoverers of berberine, although they carefully and accurately described some of its properties, do not appear to have made any analyses of their

product, and it was not till 1835 that any attempts were made to ascertain the composition of this interesting substance. In this year, Buchner and Herberger (*Annalen*, **24**, 228) published the results of an important series of experiments on this alkaloïd, together with a number of analyses of the base itself, and also of its compound with oxide of silver. These experiments led them to the supposition that berberine was represented by the formula  $C_{33}H_{36}N_2O_{12}$  ( $C = 6 : O = 8$ ).

At a later date, Fleitmann made a careful examination of berberine, and showed that instead of being a weak acid, as Buchner had suggested, it was in reality a strong base, forming with acids stable salts, and in all respects showing the properties of a well-defined alkaloïd.

Fleitmann analysed not only berberine itself but also several of its salts, and the results of his experiments led him to the conclusion that the formula proposed by Buchner was erroneous, and that the composition of this base was  $C_{12}H_{18}NO_9$  ( $C = 6 : O = 8$ ).

In the year 1861, J. Dyson Perrins (*Annalen*, Suppl. **2**, 176) published the most accurate investigation of berberine which had up to that time been made, in the course of which he analysed a large number of its salts, and showed, in a most conclusive manner, that Fleitmann's formula was inaccurate, and that the true formula was  $C_{20}H_{17}NO_4$  ( $C = 12 : O = 16$ ).

Although the analytical results obtained by Perrins agree so closely with this formula, I still thought it necessary, before starting an investigation on the constitution of this interesting alkaloïd, to repeat some of these analyses with specially purified substances, so as to leave no doubt as to the relation of the carbon, hydrogen, nitrogen, and oxygen-atoms in it. The berberine used in these experiments was purified in the following manner:—

Crude berberine hydrochloride (from Merck in Darmstadt) was recrystallised twice from water acidified with hydrochloric acid, the beautiful yellow, silky needles dissolved in a little boiling water, and the solution rendered alkaline by the addition of an excess of carbonate of soda solution.

On cooling, the liquid became filled with brownish, silky crystals. These were filtered from the dark brownish-red mother-liquor, washed with water till the washings were only slightly yellowish, and dried on a porous plate. The beautiful silky mass thus obtained was next dissolved in boiling 80 per cent. alcohol (carefully purified methylated spirits may also be used) from which, on slowly cooling, long, yellowish-brown needles separated. After repeated crystallisation from dilute alcohol, these crystals entirely lose their original brownish colour, and are at length deposited in the form of long, silky needles of an intensely yellow colour. This substance was repeatedly analysed under varying conditions, but in spite of this no

satisfactory results could be obtained. One reason for this is that the substance contains several molecules of water of crystallisation, part of which is given off slowly at ordinary temperatures and part at  $100^{\circ}$ .

The substance dried at  $100^{\circ}$  is, however, never free from water of crystallisation, and if attempts are made to drive this off at a higher temperature, slight decomposition invariably takes place sufficient to spoil the analytical results. Another reason for the difficulty experienced in obtaining concordant numbers with berberine prepared in this way, is that the substance almost invariably contains traces of chlorine.

Experience showed that the nitrate, hydriodide, and platinochloride of berberine were far more suitable for analytical examination than the base itself.

*Berberine Nitrate*,  $C_{20}H_{17}NO_4 \cdot HNO_3$ .—This salt has been described by both Fleitmann and Perrins. It is readily prepared by adding an excess of dilute nitric acid to a warm, concentrated solution of the base. The nitrate is thus precipitated as a yellow crystalline mass, which is collected, well washed with water, and repeatedly recrystallised from this solvent. In this way beautiful yellow needles were obtained which, after drying first over sulphuric acid in a vacuum and then at  $100^{\circ}$ , gave the following results on analysis:—

- I. 0.1724 gram substance gave 0.0722 gram  $H_2O$  and 0.3808 gram  $CO_2$ .  
 II. 0.1638 gram substance gave 0.0679 gram  $H_2O$  and 0.3621 gram  $CO_2$ .  
 III. 0.2056 gram substance gave 12.5 c.c. N. Bar = 760 mm.  $t = 15^{\circ}$ .

	Theory. $C_{20}H_{17}NO_4 \cdot HNO_3$ .	Found.			
		I.	II.	III.	
C. ....	60.30 p. c.	60.24	60.27	—	p. c.
H. ....	4.52 „	4.65	4.52	—	„
N. ....	7.04 „	—	—	7.16	„
O. ....	28.14 „	—	—	—	„

These numbers agree well with those previously found by Fleitmann and Perrins, but not so well with those given by Henry.

	Fleitmann.		Perrins.	Henry.	
	60.15	59.64 p. c.		59.09	59.44 p. c.
C. ...	60.15	59.64 p. c.	60.19 p. c.	59.09	59.44 p. c.
H ...	4.75	4.62 „	4.60 „	4.85	4.84 „

This salt is readily soluble in hot water, sparingly in cold, and almost insoluble in dilute nitric acid.

If the hot solution of berberine nitrate be mixed with a small quantity of ammonia, on cooling a remarkable compound separates in sparingly soluble golden plates. I have not as yet been able to determine the nature of this substance, but from the analyses already carried out it appears to have the formula  $C_{20}H_{20}N_2O_3$ .

(Found C = 55.2. H = 4.8. N = 6.80. Theory requires C = 55.55. H = 4.63. N = 6.48.)

I am at present engaged in the investigation of this substance.

*Berberine Hydr iodide*,  $C_{20}H_{17}NO_4.HI$ .—This very insoluble salt is obtained as a yellow precipitate when an aqueous solution of berberine is acidified with a few drops of aqueous hydrogen iodide—or when potassic iodide is added to a solution of nitrate of berberine. The salt was collected, well washed with water, dried on a porous plate, and recrystallised from a large quantity of boiling 80 per cent. alcohol.

In this way, beautiful satiny needles were obtained which on analysis gave the following numbers:—

I. 0.1460 gram substance gave 0.0523 gram  $H_2O$  and 0.2767 gram  $CO_2$ .

II. 0.3561 gram substance gave 0.1795 gram  $AgI$ .

	Theory. $C_{20}H_{17}NO_4.HI$ .	Found.	
		I.	II.
C .....	51.83 p. c.	51.68	— p. c.
H .....	3.88 „	3.98	— „
I .....	27.43 „	—	27.25 „

Perrins and Henry, who also analysed this salt, obtained numbers agreeing closely with the above.

	Perrins.		Henry.
C .....	51.72	51.77 p. c.	51.59 p. c.
H .....	3.92	3.96 „	4.23 „
I .....	27.02	27.12 „	25.71 „

*Berberine Platinochloride*,  $(C_{20}H_{17}NO_4)_2.H_2PtCl_6$ .—This double salt has, on account of its insolubility and suitability for determining the molecular weight of berberine, been repeatedly examined. It is readily prepared by adding platinum chloride in excess to a slightly acid solution of berberine hydrochloride. The yellow precipitate thus thrown down was collected, well washed with water, dried on a porous plate over sulphuric acid, and then at  $100^\circ$ , and analysed with the following results:—

- I. 0.2251 gram substance gave 0.0708 gram  $\text{H}_2\text{O}$ , 0.3657 gram  $\text{CO}_2$ , and 0.0406 gram Pt.  
 II. 0.6807 gram substance gave 0.1228 gram Pt.  
 III. 0.2780 gram substance gave 0.2192 gram  $\text{AgCl}$ .

	Theory. ( $\text{C}_{20}\text{H}_{17}\text{NO}_4$ ) $_2$ , $\text{H}_2\text{PtCl}_6$ .	Found.		
		I.	II.	III
C. ....	44.47 p. c.	44.31	—	— p. c.
H. ....	3.33 „	3.49	—	— „
Pt. ....	18.02 „	18.03	18.08	— „
Cl. ....	19.73 „	—	—	19.50 „

Previous analyses of this salt by Fleitmann, Perrins, and Henry gave the following results, which are in each case the mean of a number of experiments:—

	Fleitmann.	Henry.	Perrins.
C. ....	44.40 p. c.	44.38 p. c.	44.33 p. c.
H. ....	3.50 „	3.57 „	3.41 „
Pt. ....	18.11 „	17.90 „	18.21 „

This salt is almost insoluble in all the ordinary solvents. It crystallises from its solution in boiling amyl alcohol, on cooling in small, yellow needles, but it is extremely insoluble in this solvent even on boiling.

The analyses of these three salts show conclusively that the correct formula for berberine is  $\text{C}_{20}\text{H}_{17}\text{NO}_4$ . For a complete list of the various berberine salts which have from time to time been analysed by different investigators, I must refer to a paper by Hlasiwetz and Gilm (*Annalen*, Suppl. **2**, 197—201); and also to a recent paper by Ernst Schmidt (*Mittheilungen aus pharm. chem. Institut, Marburg*), which I have only lately had the opportunity of consulting.

In his researches on berberine (*loc. cit.*), Fleitmann states that it crystallises from water with  $4\frac{1}{2}$  mols.  $\text{H}_2\text{O}$ . Several analyses which I made with different samples agree rather with the formula  $\text{C}_{20}\text{H}_{17}\text{NO}_4 + 5\frac{1}{2} \text{H}_2\text{O}$ . In these experiments the berberine used was prepared by Fleitmann's method, very carefully purified by repeated recrystallisation from water, and then dried in the air on a porous plate at the ordinary temperature. Determinations of the amount of water of crystallisation given off at  $100^\circ$  gave the following results:—

- I. 1.5241 gram substance heated to  $100^\circ$  till constant lost 0.1944 gram.

- II. 0.5883 gram substance heated to  $100^{\circ}$  till constant lost 0.0702 gram.  
 III. 0.6444 gram substance heated to  $100^{\circ}$  till constant lost 0.0758 gram.  
 IV. 0.7017 gram substance heated to  $100^{\circ}$  till constant lost 0.0851 gram.

Found.	I.	II.	III.	IV.
H <sub>2</sub> O.....	12.7	11.9	11.9	12.1 p. c.

Complete analyses of different preparations of berberine dried at  $100^{\circ}$  till constant gave the following numbers:—

- I. 0.2385 gram substance gave 0.1239 gram H<sub>2</sub>O and 0.5550 gram CO<sub>2</sub>.  
 II. 0.2095 gram substance gave 0.1041 gram H<sub>2</sub>O and 0.4877 gram CO<sub>2</sub>.  
 III. 0.1316 gram substance gave 0.0666 gram H<sub>2</sub>O and 0.3032 gram CO<sub>2</sub>.  
 IV. 0.3130 gram substance gave 11.4 c.c. N.  $t = 16.5^{\circ}$ . Bar. = 736 mm.

	Theory. C <sub>20</sub> H <sub>17</sub> NO <sub>4</sub> + 2½H <sub>2</sub> O.	Found.			
		I.	II.	III.	IV.
C.....	63.16 p. c.	63.08	63.49	63.83	— p. c.
H....	5.78 „	5.77	5.52	5.66	— „
N....	3.68 „	—	—	—	3.72 „

From these analyses, it seems probable that berberine dried at  $100^{\circ}$  still contains  $2\frac{1}{2}$  mols. H<sub>2</sub>O, and that the air-dried substance originally contained  $5\frac{1}{2}$  mols. H<sub>2</sub>O, 3 of which are driven off at  $100^{\circ}$ . This would require a loss of 12.4 per cent., which agrees approximately with the numbers given above.

Hermann Schreiber (*Dissertation Marburg*, 1888) is of opinion that berberine crystallises with 6 mols. H<sub>2</sub>O, all of which is expelled at  $100^{\circ}$  in a stream of hydrogen.

#### *Properties of Berberine.*

Berberine crystallises from water in brilliant, yellow needles, which when dried in the air have a fine silky lustre. The base itself and also its salts are remarkable for their excessively bitter taste; when warmed, they emit a faint but peculiar odour strongly resembling that of ordinary quinone.

When heated to  $100^{\circ}$ , the yellow berberine crystals gradually lose their lustre, and become yellowish-brown, at  $110^{\circ}$  the change is very



rapid, and at temperatures above  $160^{\circ}$  total decomposition soon sets in with formation of a brownish-black mass, from which I have not as yet been able to obtain anything of a crystalline nature.

On account of this behaviour of berberine when heated, I have not made any attempts to determine its melting point. Fleitmann (*loc. cit.*) gives as the melting point of berberine  $120^{\circ}$ , but this is certainly too low.

If bromine-water be added to even very dilute solutions of berberine, a yellow precipitate is produced, which on standing rapidly becomes darker. If the product is collected and washed with dilute sulphurous acid, a yellowish-orange mass is obtained, crystallising from large quantities of boiling water in needles, which appear to consist of the hydrobromide of a new base. Schreiber (*loc. cit.*, p. 38) considers this substance to be simply berberine hydrobromide.

Berberine not only combines with acids to form salts, but it also gives peculiar compounds with alkalis. The addition of methyl alcoholic potash to a strong solution of berberine in alcoholic potash produces a pinkish-white, amorphous precipitate, which contains considerable quantities of inorganic matter. The analyses of this compound have not as yet given satisfactory results.

Berberine does not appear to combine either with hydroxylamine or phenylhydrazine, and although the alkaloid dissolves readily in a mixture of oxychloride and pentachloride of phosphorus, no change seems to take place even when the mixture is allowed to remain for a long time at ordinary temperatures.

Before publishing the details of the experiments which have been made in this direction, I propose to confirm the results already obtained, by using, instead of the alkaloid itself, some salt, such as the nitrate, which contains no water of crystallisation.

In its behaviour towards reagents, berberine shows the following characteristic reactions:—

It dissolves in concentrated sulphuric acid, forming a yellow solution, which on warming turns olive-green.

Very dilute solutions of berberine give with chlorine-water a decided brownish-red coloration, whilst strong solutions are coloured intensely by this reagent. Reducing agents, such as tin and hydrochloric acid, destroy this colour, which, however, reappears on the further addition of chlorine-water.

Concentrated nitric acid dissolves berberine, forming a dark, reddish-brown solution, from which water precipitates a yellow, flocculent mass, partly soluble in ammonia. If the brown-red solution in nitric acid be warmed, oxidation rapidly sets in with evolution of abundance of red fumes, and formation of a yellow solution which contains ber-

beronic acid, oxalic acid, and other products. Potassium ferrieyanide in alkaline solution gives with berberine a yellow precipitate, being itself for the most part reduced to ferroeyanide.

If a trace of berberine be boiled for a short time with concentrated aqueous hydrogen iodide, the product diluted with water and rendered slightly alkaline by the addition of ammonia, an intense blackish-violet coloration is produced.

Berberine is also characterised by the insolubility of some of its compounds, as, for instance, its hydriodide, platinochloride, aurochloride, chromate, &c., whilst a number of soluble salts, such as the nitrate, are rendered almost insoluble by the addition of a mineral acid.

A solution of iodine in potassic iodide gives with extremely small quantities of berberine salts a brownish precipitate of the periodide,  $C_{20}H_{17}NO_4, HI, I_2$ . If the precipitation be carefully conducted in warm alcoholic solution, beautiful, shining, green plates separate.

*Berberine Hydrochloride*,  $C_{20}H_{17}NO_4, HCl + 2H_2O$ .—This beautiful salt crystallises from water in long, yellow needles. As mentioned at the commencement of the paper, this salt, in spite of its beautiful appearance, does not give very satisfactory results on analysis.

If attempts are made to dry it at  $100^\circ$ , in a short time the yellow colour of the crystals gradually changes to brownish-yellow, and then to brownish-red, small quantities of hydrochloric acid being invariably lost during the operation. Analysis of the pure substance dried over sulphuric acid gave numbers agreeing fairly well with those required by the formula  $C_{20}H_{17}NO_4, HCl + 2H_2O$ .

- I. 0.2075 gram substance gave 0.1057 gram  $H_2O$  and 0.4461 gram  $CO_2$ .  
 II. 0.1557 gram substance gave 0.0792 gram  $H_2O$  and 0.3383 gram  $CO_2$ .  
 III. 0.5091 gram substance gave 16.5 c.c. N. Temp. =  $17^\circ$ . Bar. 727 mm.

	Theory. $C_{20}H_{17}NO_4, HCl + 2H_2O$ .	Found.		
		I.	II.	III.
C .....	58.89 p. c.	58.63	59.25	— p. c.
H .....	5.39 „	5.66	5.65	— „
N .....	3.43 „	—	—	3.63 „

The difficulty in obtaining good results in the analysis of this substance is partly accounted for by the fact that the salt dried as above is so excessively hygroscopic as to render it very difficult to weigh it out with the necessary degree of accuracy.

As the result of a number of careful analyses, E. Schmidt (*loc. cit.*,

p. 54) has shown that berberine hydrochloride crystallises from dilute alcohol with 4 mols.  $\text{H}_2\text{O}$ .

*Oxidation of Berberine with Potassium Permanganate.*

In most of the investigations on the constitution of the alkaloids which have up to the present time been carried out, it has been found that the careful examination of the behaviour of this class of substances towards oxidising agents has almost invariably given interesting results, and in some cases very important clues as to their structure.

The molecule of the alkaloid is usually split up, yielding acids of much simpler constitution, such as hemipinic acid (from narcotine), carboxylic acids of pyridine, quinoline, and their derivatives (in the case of quinine, cinchonine, &c.), &c., although in some cases acids containing nearly the same number of carbon-atoms as the alkaloid employed are obtained.

One of the most remarkable examples of the value of careful oxidation in investigating an alkaloid is that of papaverine, from which by the use of potassium permanganate under various conditions Goldschmiedt was able to obtain among other substances papaverinic, veratric, hemipinic, pyridinetricarboxylic, and dimethyl-oxy-cinchoninic acids and papaveraldine.

Experiments on the oxidation of berberine with potassic permanganate have already been made by E. Schmidt and C. Schilbach (*Arch. Pharm.* [3], **25**, 164—170; *Abstr.*, 1887, 604), who obtained thus considerable quantities of hemipinic acid.

In some preliminary experiments on berberine made early in 1887, I also obtained hemipinic acid in considerable quantities by the oxidation of berberine with alkaline permanganate, and lately, in view of the remarkable results obtained by Goldschmiedt in his examination of hemipinic and isohemipinic acids (*Monats.*, 1888, 861), I have again very carefully studied this decomposition, partly with the object of determining whether the acid obtained is simply hemipinic acid or a mixture of this acid with metahemipinic acid, and partly from a desire to obtain some substance intermediate between berberine and this acid, which might afford some clue to the constitution of the alkaloid.

The first experiments were carried out almost exactly in the way Goldschmiedt recommends in his first paper on papaverine (*Monats.*, 1885, 1112).

30 grams of pure berberine hydrochloride were dissolved in 1 litre of boiling water, the salt decomposed by the addition of 6 grams of potassic carbonate, and then oxidised by slowly running

in 150 grams of potassic permanganate dissolved in 3 litres of hot water. At first the oxidation is very rapid, but as soon as about two-thirds of the permanganate have been added, decolorisation takes place much more slowly, continued boiling being necessary to remove the last traces of the oxidiser.

At the end of this operation, the product was saturated with carbonic acid, filtered through a cloth filter, and the manganese precipitate well pressed; this was then carefully extracted by repeated boiling with water, and pressing in a vice. The filtrate and washings were evaporated to dryness, the residue pulverised and repeatedly exhausted with boiling absolute alcohol (or purified methylated spirits), the alcoholic solution distilled, and the residue, after freeing it from the last traces of alcohol by gently warming on a water-bath, was dissolved in a little water and filtered. On acidifying with dilute sulphuric acid, the brown aqueous solution deposits a small quantity of a resinous precipitate, from which, however, nothing crystalline could be obtained. It was removed by filtration, the clear filtrate extracted 20 times with pure ether, the ethereal solution dried over calcic chloride and evaporated, and the brownish residue thus obtained was allowed to remain for some days over sulphuric acid in a vacuum. The crude semi-solid mass was then roughly purified by spreading it on a porous plate, and afterwards repeatedly recrystallised from boiling water. In this way beautiful transparent crystals were obtained, which on analysis gave numbers agreeing with those required for hemipinic acid:—

0.1827 gram substance gave 0.0720 gram  $\text{H}_2\text{O}$  and 0.3550 gram  $\text{CO}_2$ .

	Theory. $\text{C}_{10}\text{H}_{10}\text{O}_6$ .	Found.
C .....	53.10 per cent.	52.99 per cent.
H .....	4.42     ,,	4.38     ,,
O .....	42.48     ,,	42.73     ,,

Determination of water of crystallisation:—

0.8878 gram of substance heated to  $100^\circ$  till constant lost 0.1236 gram = 13.92 per cent. Theory for  $\text{C}_{10}\text{H}_{10}\text{O}_6 + \text{H}_2\text{O} = 13.74$  per cent.

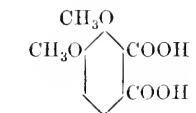
Considerable difference of opinion exists as to the melting point of hemipinic acid. Wegscheider (*Monats.*, **3**, 351) gives  $175\text{--}179^\circ$  for the acid from narcotine; Liebermann (*Ber.*, **19**, 2279),  $180\text{--}181^\circ$ , and Grüne (*Ber.*, **19**, 230)  $180^\circ$ , whereas E. Schmidt and Schilbach (*Arch. Pharm.*, **225**, 164) found for the hemipinic acid prepared by them from berberine, and also for the acid from narcotine, the low melting point  $160\text{--}161^\circ$ . Goldschmiedt, who has lately most

carefully re-examined the hemipinic acid from narcotine, found that although when rapidly heated it melted at  $172-175^{\circ}$  with decomposition into anhydride and water, yet when slowly heated it melted at  $160-161^{\circ}$ . I have repeated these experiments with the hemipinic acid from berberine, and although I can corroborate the experience of Goldschmiedt that the melting point varies considerably according to the rapidity of the heating, still I have never been able to observe a melting point lower than  $170^{\circ}$ . When heated moderately rapidly, the acid obtained as above melts regularly at  $177-178^{\circ}$  with decomposition.

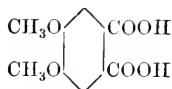
In studying the action of small quantities of permanganate on berberine, I subsequently obtained an acid,  $C_{10}H_{10}O_6$ , of totally different appearance, which melted at  $159-160^{\circ}$  with decomposition, and thus showed all the properties of hemipinic acid from narcotine.

As I was, therefore, not quite satisfied that the acid obtained as described above, melting at  $177-178^{\circ}$ , was hemipinic acid and not metahemipinic acid, I carefully examined my product in the way suggested by Goldschmiedt (*Monats.*, 1888, 870).

In his researches on papaverine, Goldschmiedt obtained by the oxidation with alkaline permanganate an acid of the formula  $C_{10}H_{10}O_6$ , which from its properties (m. p.  $174-175^{\circ}$ , water of crystallisation, &c.) he at first supposed to be identical with the hemipinic acid from narcotine. The further study of the constitution of papaverine, however, showed that these two acids could not be identical, but must be isomeric merely, a conclusion which was borne out by the further examination of their properties. As both these acids on fusion with potash give protocathecinic acid, and both are orthocarboxylic acids, their constitution must be represented by the formulæ—



Hemipinic acid from  
narcotine.



Metahemipinic acid from  
papaverine.

In examining the hemipinic acid from berberine, I first made a determination of the methoxyl-groups according to Zeisel's method (decomposition with hydrogen iodide and determination of the amount of methyl iodide formed by leading into an alcoholic solution of silver nitrate, and estimating the silver iodide precipitated (*Monats.*, 1883, 704), with the following results:—

0.2740 gram substance dried at  $100^{\circ}$  gave 0.7350 gram AgI.

	Found.	Theory for $C_{10}H_{10}O_6$ .
$OCH_3$ . . .	27.74 per cent.	27.43 per cent.

In order, then, to prove that the acid from berberine was a derivative of pyrocatechol, a small quantity was decomposed by fusion with potash. 2 grams of the pure acid was dissolved in a little potash, the solution evaporated to dryness, and the residue fused in a silver dish with 50 grams of pure caustic potash and a little water for about half an hour. The resulting almost colourless melt was dissolved in water and acidified with dilute sulphuric acid, during which operation the solution became first blue, then violet, and lastly reddish, but remained clear. It was extracted several times with ether, the ethereal solution dried over calcic chloride, and the ether distilled off; in this way, a crystalline residue was obtained which, after recrystallising once or twice from a little water, gave the following results on analysis:—

0.1217 gram substance dried at  $100^\circ$  gave 0.0442 gram  $H_2O$  and 0.2436 gram  $CO_2$ .

	Theory. $C_7H_6O_4$ .	Found.
C . . . . .	54.55 per cent.	54.59 per cent.
H . . . . .	3.89     ,,	4.03     ,,
O . . . . .	4.56     ,,	4.48     ,,

A determination of the water of crystallisation gave the following results:—

0.3326 gram of air-dry substance dried at  $100^\circ$  lost 0.0347 gram.

	Theory. $C_7H_6O_4 + H_2O$ .	Found.
$H_2O$ . . . . .	10.46 per cent.	10.43 per cent.

This acid has, therefore, the composition of protocatechuic acid, with which it agrees in all its properties.

It crystallised from hot water in needles melting at  $195$ — $196^\circ$ . The aqueous solution gives with ferric chloride a deep, emerald-green coloration, which, on the careful addition of sodic carbonate solution, becomes first blue, then violet, and at last red. It reduces an ammoniacal silver solution at once, gives with lead acetate a white precipitate soluble in acetic acid, and on heating is decomposed into carbonic anhydride and a white crystalline sublimate which shows all the reactions of pyrocatechol. These reactions, however, do not determine whether the acid obtained from berberine is hemipinic or meta-hemipinic acid, as both these acids contain two methoxyl-groups, and

both on fusion with potash yield protocathecinic acid. These two acids can, however, be readily distinguished by conversion into their ethylimides; the ethylimide of hemipinic acid melting at  $96^{\circ}$ , whilst that of metahemipinic acid melts at  $226-227^{\circ}$ .

In order to prepare the ethylimide of the acid from berberine, the pure substance was dissolved in an aqueous solution of ethylamine, the solution evaporated to dryness on a water-bath, and the residue distilled from a small retort. The solid distillate was dissolved in a little boiling methyl alcohol and allowed to stand, when beautiful needle-shaped crystals were obtained, which on analysis gave the following numbers:—

0.1753 gram substance gave 9.7 c.c. N. Bar. = 760 mm.  $t = 14.5^{\circ}$ .

	Theory. $C_{12}H_{13}NO_4$	Found.
N. ....	5.96 per cent.	6.09 per cent.

This ethylimide melts at  $94-95^{\circ}$ , but when recrystallised from water, at  $96^{\circ}$ , and shows all the properties of ethylhemipinimide, prepared by Liebermann by the action of ethyl iodide on the potassium-derivative of hemipinimide. It is therefore proved beyond doubt that hemipinic acid from berberine is identical with that obtained from narcotine.\*

Besides hemipinic acid, there are small quantities of at least two other acids formed when berberine is oxidised with permanganate in the proportions given above, both of which are present in the potassic carbonate residues, from which the potash salt of hemipinic acid has been extracted with alcohol. These residues were dissolved in a small quantity of water, neutralised with acetic acid, and treated with acetate of copper. On long standing in a warm place, the green solution thus produced deposited a small quantity of a light bluish-green precipitate. This was collected, well washed with water, and decomposed by passing sulphuretted hydrogen through the salt suspended in boiling water; the filtrate, on evaporation, gave a small quantity of a crystalline residue which on examination was found to contain nitrogen.

On recrystallising from water, small nodular crystals were obtained, melting at  $238-242^{\circ}$ . These gave on analysis the following numbers:—

0.2629 gram substance gave 14.5 c.c. N. Bar = 759.  $t = 14^{\circ}$ .

	Theory. $C_8H_5NO_6 + H_2O$	Found.
N. ....	6.11 per cent.	6.48 per cent.

\* This confirms the results obtained by E. Schmidt (*loc. cit.*, 63—73).

Unfortunately the amount of this acid obtained by this reaction was too small to allow of further experiments being made to determine its composition, but from its melting point and analysis it would appear to be either carboeinchomeronic acid or berberonic acid. This is the more probable, as berberine when oxidised by nitric acid yields berberonic acid. It is interesting to notice that E. Smith and C. Schilbach (*Arch. Pharm.* [3], 25, 164—170) in their experiments on the oxidation of berberine with permanganate, also noticed the formation of a nitrogenous acid, crystallising in nodular crystals, and melting at 218—220°. The silver salt, however, gave numbers showing this acid to be a pyridinemonocarboxylic acid (nicotinic acid?).

The mother-liquor from the copper salt was treated with sulphuretted hydrogen, filtered from the precipitated sulphide of copper, and subacetate of lead added so long as a precipitate was produced. The lead salt was collected, well washed, suspended in water, decomposed with sulphuretted hydrogen, and the filtered solution evaporated to dryness.

The residue, when dissolved in a small quantity of boiling water, and the solution allowed to cool slowly, deposited, after some time, a quantity of crystals; these, on examination, were found to consist of two distinct substances, the one crystallising in thick, brownish prisms, and the other in long, colourless needles. The brownish prisms were mechanically separated, recrystallised several times from water, and the colourless crystalline mass thus obtained dried at 100°, and analysed with the following result:—

0.1932 gram substance gave 0.0777 gram  $H_2O$  and 0.3763 gram  $CO_2$ .

	Theory $C_{10}H_{10}O_6$ .	Found.
C .....	53.10 per cent.	53.12 per cent.
H .....	4.42 „	4.47 „
O .....	42.48 „	42.41 „

As this substance melted at 177—178°, there can be no doubt that it was simply hemipinic acid, with which it agreed in all its reactions.

The needle-shaped crystals obtained from the lead salt together with the hemipinic acid, after recrystallisation from water, were found to consist of pure oxalic acid. It is very remarkable that in the oxidation of berberine with alkaline permanganate so little oxalic should be formed. The amount actually obtained from 60 grams of berberine was but little more than 3 grams.

From the above it will be seen that berberine, when oxidised with an excess of potassium permanganate, yields principally hemipinic



acid, the other oxidation products isolated being formed only in very small quantity. In this respect, berberine differs very widely from papaverine, which, under similar conditions, yields a number of important decomposition products, such as papaverinic acid,  $C_{16}H_{13}NO_7$ , veratrinic acid,  $C_9H_{10}O_4$ , methemipinic acid,  $C_{10}H_{10}O_6$ ,  $\alpha$ -pyridine-tricarboxylic acid,  $C_5H_5NO_6$ , &c., all of which are found in considerable quantity in the product of the oxidation. The reason for this is that berberine and its derivatives are so very readily oxidised, that unless a limited amount of permanganate is used, and the oxidation very carefully carried out, the whole molecule is split up, yielding principally hemipinic acid. As the result of a very large number of experiments carried out under a great variety of conditions, it has, however, been found possible to arrest the oxidation before it has gone as far as hemipinic acid, and in this way several new substances have been isolated, the study of which it is hoped will furnish some important clue as to the constitution of this interesting alkaloid.

In experimenting on the formation of these new derivatives I have found it necessary to work with small quantities at a time (never more than 7 grams of berberine in one operation), as when large quantities are used, even under precisely similar conditions of temperature and amount of oxidiser, very small yields are obtained.

The best results have been obtained with the following quantities:—

5 grams berberine (dried at the ordinary temperature).

9 „ „ potassic permanganate.

$1\frac{1}{2}$  „ „ carbonate.

The potassic permanganate and carbonate are dissolved in half a litre of water of  $90^\circ$ , and the solution very slowly run through a separating funnel or burette, into a hot solution ( $90^\circ$ ) of the berberine (in a quarter of a litre of water), the whole being well stirred during the operation. As soon as all the permanganate has been added (the oxidation requires about 10—15 minutes), the product is transferred to a flask, cooled well under the tap, and the manganese precipitate brought into solution by passing a slow stream of sulphurous acid into the mixture. In this way a slightly yellowish liquid is obtained, in which are suspended small, yellow, flocculent particles. These are collected, well washed with water, and freed from the last traces of mother-liquor by spreading them on a porous plate. The purification of the resulting amorphous yellow mass which contains at least three new substances, is a very difficult operation, and has, up to the present, only been successfully carried out when the following conditions have been carefully observed.

The well washed residue is suspended in water and well agitated

at a temperature of about  $40^{\circ}$ , with a slight excess of sodic carbonate, by which treatment the crude product is separated into two portions, the one soluble, the other insoluble in carbonate of soda; these are separated by filtration.

The new acid contained in the brownish-coloured filtrate is deposited on the addition of an acid in the form of an amorphous yellow precipitate, which, on account of the presence of a quantity of a resinous substance, can only with difficulty be obtained in a crystalline condition. The method of purification which has given the best results is the following:—The solution in sodic carbonate is nearly neutralised with dilute sulphuric acid, and the new acid fractionally precipitated in three fractions by running into the well-stirred solution a fine stream of very dilute sulphuric acid. The first fraction should be about one-fourth, the second one-half, the third one-fourth of the whole. The second fraction is carefully washed, dried on a porous plate, dissolved in a little methyl alcohol, and the solution transferred to a flat dish, and allowed to evaporate completely at the ordinary temperature. During the evaporation, the new acid separates in yellow nodular masses, covered with a transparent resin, which is invariably deposited along with the crystals. The resulting mixture of acid and resin is scraped off the sides of the dish and well kneaded between the fingers with a small quantity of methyl alcohol. In this way the resin is removed, leaving the warty masses almost entirely undissolved. The purified product is now dissolved in a small quantity of boiling methyl alcohol, from which it is deposited on cooling in almost colourless nodular masses, which, after repeated recrystallisation, gave the following results on analysis:—

- I. 0.1511 gram substance gave 0.0602 gram  $H_2O$  and 0.3192 gram  $CO_2$ .  
 II. 0.1421 gram substance gave 0.0552 gram  $H_2O$  and 0.3000 gram  $CO_2$ .  
 III. 0.3633 gram substance gave 10.4 c.c. N.  $t = 11^{\circ}$ . Bar. = 727 mm.

	Theory.		Found.			
	$C_{20}H_{17}NO_9$ .	$C_{20}H_{19}NO_9$ .	I.	II.	III.	
C . . . .	57.83	57.55	57.61	57.58	—	per cent.
H . . . .	4.10	4.55	4.43	4.47	—	„
N . . . .	3.37	3.36	—	—	3.40	„
O . . . .	34.70	34.53	—	—	—	„

It is as yet very difficult to decide whether this new substance has the formula  $C_{20}H_{17}NO_9$  or  $C_{20}H_{19}NO_9$ , but for various reasons I am

inclined, in the meantime, to adopt the latter formula, leaving the definite settlement of this point to further experimental proof.

This substance is readily soluble in ethyl and methyl alcohol and in acetic acid, but only sparingly in benzene, toluene, and ether, and almost insoluble in light petroleum, chloroform, ethyl acetate, and cold water. It is, however, best purified by recrystallisation from methyl alcohol, from which it is deposited, on long standing, either in warty masses or in small plates.

Considerable difficulty was experienced in determining the melting point of this new substance. When rapidly heated, it softens at about  $138-140^{\circ}$ , and then melts completely at  $141-142^{\circ}$  with evolution of gas. At  $150-155^{\circ}$  it again becomes solid, and on further heating melts again between  $195^{\circ}$  and  $200^{\circ}$ .

The pure compound,  $C_{20}H_{19}NO_9$ , dissolves readily in alkalis and in alkaline carbonates.

The barium salt was prepared by dissolving the acid in baryta-water, removing the excess of the latter by passing carbonic anhydride through the boiling solution, filtering, and evaporating on a water-bath. In this way a quantity of an almost colourless crystalline barium salt was obtained which, after washing with a little water and drying first over sulphuric acid in a vacuum and then at  $100^{\circ}$ , gave the following results on analysis:—

0.4598 gram substance gave 0.1926 gram  $BaSO_4$ .

Theory.		Found.	
$C_{20}H_{17}NO_9Ba$ .			
Ba ..	24.82 per cent.	Ba ..	24.63 per cent.

The neutral solution of the ammonium salt of this acid gives with *nitrate of silver* a white, gelatinous precipitate, soluble in a large quantity of boiling water: with *cupric acetate* a beautiful bluish-green precipitate, and, with *acetate of lead*, a white, gelatinous precipitate. Fused with a small quantity of pure caustic potash, this substance is readily decomposed, yielding an almost colourless melt which, when dissolved in water, acidified with sulphuric acid, and extracted with ether, gives a crystalline acid readily soluble in water. The solution of this acid gives with ferric chloride a deep-green coloration, changing to violet and then to deep red on the addition of sodic carbonate. As it also gives with acetate of lead a white precipitate, and readily reduces ammoniacal silver solution, it is probable that this substance is either berberinic acid or protocatchuic acid.

The residual product of the oxidation of berberine, insoluble in sodic carbonate, obtained as described above, contains, besides a quantity of a resinous substance, two new compounds which are separated in the following way:—

The crude, brownish product is well washed, first with a dilute solution of sodic carbonate, then several times with water, dried on a porous plate, and dissolved in a small quantity of boiling 90 per cent. acetic acid (5 grams of substance require about 20 grams of acetic acid). This solution on cooling gradually deposits a considerable quantity of a crystalline substance. At the end of 48 hours, this is collected, washed with a little glacial acetic acid, and purified by repeated recrystallisation from this solvent.\* It is thus obtained in flat, glittering plates, with a remarkable silky lustre: these after drying, first on a porous plate and then at  $100^{\circ}$ , gave the following results on analysis:—

- I. 0.2001 gram substance gave 0.0800 gram  $H_2O$  and 0.4387 gram  $CO_2$ .
- II. 0.1395 gram substance gave 0.0569 gram  $H_2O$  and 0.3053 gram  $CO_2$ .
- III. 0.1354 gram substance gave 0.0550 gram  $H_2O$  and 0.2971 gram  $CO_2$ .
- IV. 0.1560 gram substance gave 0.0620 gram  $H_2O$  and 0.3433 gram  $CO_2$ .
- V. 0.3773 gram substance gave 11.2 c.c. N ( $t = 13^{\circ}$ . Bar. = 760 mm.).
- VI. 0.3372 gram substance gave 10.6 c.c. N ( $t = 13.5^{\circ}$ . Bar. = 737 mm.).

	Theory. $C_{20}H_{17}NO_8$ .	Found.					
		I.	II.	III.	IV.	V.	VI.
C . . . .	60.15 p. c.	59.87	59.69	59.77	60.02	—	— p. c.
H . . . .	4.26 „	4.44	4.53	4.51	4.41	—	„
N . . . .	3.51 „	—	—	—	—	3.50	3.58 „
O . . . .	32.08 „	—	—	—	—	—	„

This substance melts at  $236-237^{\circ}$ . It is readily soluble in hot acetic acid, from which it crystallises on cooling in beautiful glittering plates, but is only sparingly soluble in ethyl and methyl alcohol, benzene, toluene, light petroleum, and acetone, even on boiling. Although insoluble in alkaline carbonates, this substance dissolves readily in warm solutions of ammonia, caustic potash, &c., forming well-defined salts. If the solution in ammonia be allowed to evaporate over sulphuric acid, a very curious jelly-like ammonium salt is deposited, which gradually dries up to a mass resembling dried albumin. This dissolves readily in water, and the solution gives with reagents some very characteristic salts.

\* The mother-liquors contain considerable quantities of a second neutral substance, which will be described further on.

*Nitrate of silver* gives a white, gelatinous precipitate which is readily soluble in hot water, but only sparingly in cold; it could not be recrystallised, as it somewhat readily decomposes on warming with water. A small quantity of this salt was prepared, well washed with cold water, dried on a piece of porous plate over sulphuric acid in a vacuum, and analysed with the following results:—

- I. 0.1996 gram substance gave 0.0560 gram  $H_2O$ , 0.2547 gram  $CO_2$ , and 0.0623 gram Ag.  
 II. 0.3286 gram substance gave 0.1023 gram Ag.

	Theory. $C_{20}H_{15}NO_8Ag_2 + 4H_2O$ .	Found.		p. c.
		I.	II.	
C . . . . .	35.04	34.80	—	
H . . . . .	3.35	3.12	—	
Ag . . . .	31.40	31.22	32.13	

From this analysis it would appear as though the neutral substance,  $C_{20}H_{17}NO_8$ , when dissolved in alkalis took up 4 mols.  $H_2O$ , forming a bibasic acid of the formula  $C_{20}H_{25}NO_{12}$ . It is, however, much more probable that the silver salt when prepared as above contains water of crystallisation, as is the case, for example, with the silver salt of papaverinic acid, which crystallises with  $2-2\frac{1}{2}$  mols.  $H_2O$ . The formula of the acid formed by dissolving the substance  $C_{20}H_{17}NO_8$  in alkalis, can therefore only be accurately determined by the analysis of some other of its salts, with the investigation of which I am at present engaged.

The solution of the ammonium salt of this acid gives with *acetate of copper* a splendid, light bluish-green precipitate, and with *acetate of lead* a white, gelatinous precipitate which dissolves somewhat sparingly in boiling water. The chlorides of *barium* and *calcium* give no precipitate in the cold; on boiling, white, amorphous salts are precipitated.

The mother-liquors from the precipitation of the substance  $C_{20}H_{17}NO_8$  contain, besides small traces of this sparingly soluble substance, a considerable quantity of a second neutral substance which is much more readily soluble. To isolate this, the dark-brown acetic acid solution is heated to boiling, diluted with one-fourth of its bulk of boiling water, and allowed to stand for 24 hours. The crystals which separate are collected, the mother-liquor again treated as above, and the operation repeated until no more crystals separate. In this way nearly the whole of the new substance crystallises out in yellowish plates, whereas if too much water be added at first the crystals are invariably mixed with a black, tarry substance which hinders their subsequent purification. The crude substance thus obtained can now

easily be purified by recrystallisation, once from dilute acetic acid and twice from pure alcohol. From the hot, alcoholic solution it is deposited on cooling in beautiful colourless plates with a pearly lustre. For analysis the substance was dried at  $100^{\circ}$ .

- I. 0.1372 gram substance gave 0.0540 gram  $H_2O$  and 0.3155 gram  $CO_2$ .  
 II. 0.1792 gram substance gave 0.0741 gram  $H_2O$  and 0.4093 gram  $CO_2$ .  
 III. 0.1395 gram substance gave 0.0584 gram  $H_2O$  and 0.3213 gram  $CO_2$ .  
 IV. 0.1680 gram substance gave 0.0720 gram  $H_2O$  and 0.3852 gram  $CO_2$ .  
 V. 0.3070 gram substance gave 10.1 c.c. N ( $t = 15^{\circ}$ . Bar. = 742 mm.).  
 VI. 0.2493 gram substance gave 8.2 c.c. N ( $t = 18.5^{\circ}$ . Bar. = 759 mm.).

	Theory. $C_{20}H_{17}NO_7$ .	Found.					
		I.	II.	III.	IV.	V.	VI.
C . . . .	62.66 p. c.	62.71	62.61	62.81	62.53	—	— p. c.
H . . . .	4.43 „	4.38	4.70	4.65	4.76	—	— „
N . . . .	3.66 „	—	—	—	—	3.75	3.80 „
O . . . .	29.24 „	—	—	—	—	—	—

This new compound, which from the analysis appears to have the formula  $C_{20}H_{17}NO_7$ , melts at  $150^{\circ}$ . It is readily soluble in hot methyl and ethyl alcohol, but only sparingly soluble in these liquids in the cold. It dissolves with difficulty in boiling water, and the solution on slowly cooling deposits the substance in beautiful, glittering plates, which resemble anthracene in appearance; if rapidly cooled, however, the aqueous solution becomes milky before crystallising. It is also readily soluble in hot, but almost insoluble in cold benzene and toluene. If this substance is not quite pure, its solutions fluoresce in a most beautiful way, reminding one strongly of a dilute solution of fluoresceïn.

The substance  $C_{20}H_{17}NO_7$  does not dissolve in alkalis in the cold, and only very slowly on boiling. The solution in hot, strong caustic potash on cooling deposits what appears to be the unchanged substance, but as the substance is more soluble in caustic potash than in water, it is possible that it forms with alkalis very unstable salts. Fused with a little potash, the substance  $C_{20}H_{17}NO_7$  yields what appears to be protocatechuic acid (? berberinic acid). In studying this decomposition, about  $\frac{1}{4}$  of a gram of substance was gently fused with 2 grams of potash and a little water in a thick test-tube. The crystals dissolved at once with evolution of quantities of a pungent

gas, which resembled methylamine or ethylamine rather than ammonia. The colourless residue dissolved in water with a reddish colour, and on acidifying and extracting with ether, a colourless crystalline substance was obtained, which showed all the properties of protocatechuic acid. The aqueous solution gave with ferric chloride a deep-green coloration, which on the addition of sodic carbonate became first blue, then violet, and at last red. On the addition of acetate of lead to the aqueous solution, a white precipitate was obtained, soluble in acetic acid.

The substance  $C_{20}H_{17}NO_7$  dissolves in strong nitric acid with a deep orange colour, and in warm sulphuric acid forming a deep violet-black solution. The addition of strong hydrochloric acid causes the crystals to turn yellow without dissolving them, and if a drop of hydrochloric acid be added to the alcoholic solution of the substance the solution is coloured slightly yellow, and acquires a bluish-green fluorescence.

In order to further control the formula of the substance  $C_{20}H_{17}NO_7$ , its molecular weight was determined by Raoult's method, with the following result:—

Substance taken .....	0.7558 gram.
Acetic acid .....	42.1296 „
Melting point of acetic acid.....	16.447°
„ of mixture .....	16.263
Depression of melting point.....	0.184

Molecular weight of substance found from the above data 380

Theory for  $C_{20}H_{17}NO_7$  ..... 383

The yield of crude, dry, yellow substance obtained by the oxidation of 200 grams of berberine as described above is about 70 grams, of which 12 grams are insoluble, and 55 grams soluble in a solution of sodic carbonate. These numbers show clearly that a large portion of the products of the oxidation must be contained in the filtrate from the yellow substance. In order to test this, the yellow solution was evaporated over a free flame, with occasional addition of a little aqueous sulphurous acid, until the inorganic salts commenced to separate as a crust on the surface. The liquid was then allowed to cool, filtered from the crystalline matter, and again evaporated, the operation being repeated until the solution from the oxidation of 200 grams of berberine was reduced in bulk to 1 litre. The brownish product was then extracted 20 times with ether, the ethereal solution dried over calcic chloride, and the ether distilled off until about 150 c.c. remained.

During this operation a quantity of a white, crystalline substance separates, which after collecting, washing with a little ether, and

drying on a porous plate, presented the appearance of hard, sandy crystals. Subsequent examination showed that this product was a mixture of two substances, which are readily separated from each other by recrystallisation from water. The solution in a small quantity of boiling water deposits on cooling first of all a quantity of glittering plates, which are rapidly filtered off. On standing, the second substance separates from the mother-liquor in hard prisms.

The more insoluble substance, which is formed only in very small quantity, was purified by recrystallisation from water; the crystals, dried first over sulphuric acid in a vacuum and then at  $100^{\circ}$ , gave the following numbers on analysis:—

- I. 0.1493 gram substance gave 0.0618 gram  $H_2O$ .  
 II. 0.2907        „        ..        8.8 c.c. N;  $t = 17^{\circ}$ .    Bar. =  
                      757 mm.

	Theory. $C_{20}H_{19}O_9$ .	Found.
C .....	57.55 per cent.	57.54 per cent.
H .....	4.55        „	4.60        „
N .....	3.35        „	3.50        „
O .....	34.53        „	34.36        „

This interesting substance, which from the above analysis appears to have the constitution  $C_{20}H_{19}NO_9$ , melts at  $178-179^{\circ}$  with decomposition, due probably to loss of water. It is sparingly soluble in alcohol and ether, fairly soluble in boiling water, from which it crystallises on cooling, either in small plates, or in very small, warty masses.

At present only sufficient of this substance has been obtained for the above analyses, and subsequent investigation must show whether the constitution assigned to it is correct.

This acid has the same formula as the acid obtained from the yellow precipitate (p. 78), but as it melts  $38^{\circ}$  higher it must be isomeric, and not identical with this substance.

The crude crystals of the more soluble substance obtained, as described above, were separated from the substance  $C_{20}H_{17}NO_9$  by repeated recrystallisation from water, from which they were invariably deposited as a hard, crystalline crust on the bottom of the beaker. The air-dried crystals, when heated on a water-bath, lost scarcely any weight, showing the absence of water of crystallisation.

On analysis the following numbers were obtained:—

- I. 0.1518 gram substance gave 0.0608 gram  $H_2O$  and 0.2970 gram  $CO_2$ .  
 II. 0.1729 gram substance gave 0.0701 gram  $H_2O$  and 0.3361 gram  $CO_2$ .



	Theory. $C_{10}H_{10}O_6$ .	Found.	
		I.	II.
C . . . . .	53.10 p. c.	53.36	53.28 p. c.
H . . . . .	4.42 „	4.45	4.52 „
O . . . . .	42.48 „	42.19	42.20 „

This substance melts at  $159-160^\circ$  with decomposition, and as it gives protocathecinic acid on fusion with potash, there can scarcely be a doubt that it is hemipinic acid. It is, however, in appearance totally different from the hemipinic acid previously obtained (see p. 73). The crystals, which contain no water of crystallisation, are very soluble in hot water, and separate from the solution very slowly indeed, the deposition often being incomplete after standing for 24 hours.

The hemipinic acid obtained as described at the commencement of this chapter, and also a sample of the same substance prepared from narcotine (for which I am indebted to Dr. Goldschmiedt), crystallise rapidly with 2 mols.  $H_2O$  of crystallisation, when the hot aqueous solution is allowed to cool moderately slowly. The crystals dried at  $100^\circ$ , and heated under the same conditions as the above, melt at  $177-178^\circ$  with decomposition.

The great difference in the properties of the two preparations lead me to doubt their identity, and in order to establish this the silver salt of the acid, melting at  $159-160^\circ$ , was prepared and examined. This salt is thrown down on the addition of silver nitrate to the ammonium salt as a heavy, white precipitate. It was well washed with water, dried over sulphuric acid in a vacuum, and then analysed with the following result:—

I. 0.2928 gram substance gave 0.1430 gram Ag.

II. 0.2505 „ „ 0.1222 „

	Theory. $C_{10}H_8O_6Ag_2$ .	Found.	
		I.	II.
Ag . . . . .	49.69 p. c.	48.83	48.78 p. c.

This salt gives therefore the same numbers as those required for the silver salt of hemipinic acid.

Subsequent experiments on these two preparations of hemipinic acid make it appear probable that this substance exists in two distinct forms, the one melting at  $159-160^\circ$ , and the other at  $177-178^\circ$ . If a crystal of the latter acid be added to a warm saturated solution of the former, in some cases at least, the one modification is completely converted into the other, but this change appears only to take place under certain conditions of concentration, &c.

I hope to be able to investigate this point more completely at an early date.

*Action of Hydrogen Iodide on Berberine.*

When heated with fuming aqueous hydrogen iodide, berberine is readily decomposed with evolution of methyl iodide, and formation of a new substance, which dissolves in alkalis with a blackish-violet coloration. This preliminary experiment led me to suppose that berberine is decomposed by hydrogen iodide in a way similar to papaverine, which under this treatment is split up into papaveroline,  $C_{16}H_{13}NO_4$ , and 4 mols. of methyl iodide. In determining the constitution of berberine, it was a matter of great importance to discover the number of  $OCH_3$  groups contained in the formula  $C_{20}H_{17}NO_4$ , and this is readily done by Zeisel's method (*Monats.*, **6**, 995), which consists in decomposing the alkaloid with fuming hydrogen iodide, and determining the amount of methyl iodide formed by means of alcoholic silver nitrate. The first experiments in this direction were made with berberine itself, with the following results:—

- I. 0.2930 gram of berberine (dried at  $100-110^\circ$ ) gave 0.3990 gram AgI.
- II. 0.3315 gram of berberine (dried at  $100-110^\circ$ ) gave 0.4440 gram AgI.
- III. 0.3290 gram of berberine (dried at  $100-110^\circ$ ) gave 0.4430 gram AgI.

Theory for 2( $OCH_3$ ) groups in $C_{20}H_{17}NO_4 + H_2O$ .	Found.		
	I.	II.	III.
( $OCH_3$ ) . . . . 17.56 p. c.	18.03	17.72	17.83 p. c.

These experiments show that berberine contains only two  $OCH_3$  groups in its molecule, these two being present in the portion which on oxidation yields hemipinic acid. Owing, however, to the difficulty in determining accurately the amount of water of crystallisation present in the samples of berberine used, these results were not considered perfectly trustworthy, and in order to be quite certain similar experiments were instituted with the nitrate and hydriodide of the base, these salts being so readily obtained pure and free from water of crystallisation.

- 1. 0.3903 gram berberine nitrate, dried at  $100^\circ$ , gave 0.4669 gram AgI.

Theory for 2( $OCH_3$ ) groups in $C_{20}H_{17}NO_4.HNO_3$ .	Found.	
	( $OCH_3$ ) . . . .	15.74 per cent.
15.59 per cent.		

II. 0.4401 gram berberine hydriodide gave 0.4520 gram AgI.

Theory for 2(OCH <sub>3</sub> ) groups in C <sub>20</sub> H <sub>17</sub> NO <sub>4</sub> HI.		Found.
(OCH <sub>3</sub> ) . . . .	13.39 per cent.	13.61 per cent.

In order, if possible, to isolate the phenolic substance formed during this reaction, the experiment was carried out with larger quantities. 25 grams of pure berberine were boiled with a considerable excess of fuming aqueous hydrogen iodide in a flask connected with a reflux condenser, until evolution of methyl iodide had ceased.

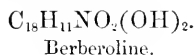
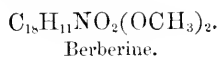
The dark-coloured solution on cooling deposited a small quantity of the new substance in the form of blackish-coloured nodules. These were collected, the solution distilled from a small retort until half had passed over and again allowed to cool, when a further quantity of solid was obtained. The crude product was well washed with water till free from hydrogen iodide, and ground to a paste in a mortar with a weak solution of sulphurous acid, to remove a small quantity of iodine. The yellowish-brown emulsion was now collected on a filter-pump, well washed with water, and extracted with boiling water containing a little sulphurous and sulphuric acids. The hot solution, after filtering from a quantity of a brown insoluble residue, deposited the new substance on cooling in beautiful orange-coloured, amorphous flocks, which entirely filled the liquid. These were collected, reprecipitated twice from hot water containing sulphurous acid, dried over sulphuric acid in a vacuum, and analysed, with the following result:—

- I. 0.1478 gram substance gave 0.0582 gram H<sub>2</sub>O and 0.3097 gram CO<sub>2</sub>.
- II. 0.1546 gram substance gave 0.0631 gram H<sub>2</sub>O and 0.3244 gram CO<sub>2</sub>.
- III. 0.4354 gram substance gave 15.2 c.c. N;  $t = 0.12$ . Bar. = 740 mm.
- IV. 0.4086 gram, decomposed by nitric acid according to Carius' method, gave 0.1314 gram BaSO<sub>4</sub>.
- V. 0.4401 gram, decomposed by nitric acid according to Carius' method, gave 0.1412 gram BaSO<sub>4</sub>.
- Ia. 0.2784 gram substance, heated to 100° till constant, lost 0.0123 gram.
- Ila. 0.2502 gram substance, heated to 100° till constant, lost 0.0112 gram.

		Found.						
Theory.		I.	II.	III.	IV.	V.		
$(C_{18}H_{13}NO_4)_2 \cdot H_2SO_4 + 2H_2O$ .								
C . . . . .	57.75 p. c.	57.12	57.22	—	—	—	p. c.	
H . . . . .	4.28 „	4.37	4.60	—	—	—	„	
N . . . . .	3.74 „	—	—	4.01	—	—	„	
H <sub>2</sub> SO <sub>4</sub> . .	13.10 „	—	—	—	13.52	13.45	„	
H <sub>2</sub> O . . . .	4.81 „	4.43	4.47	—	—	—	„	

This substance is therefore the sulphate of a base of the formula  $C_{18}H_{13}NO_4$ , for which I propose the name *berberoline*.

This base is formed from berberine simply by substituting hydrogen for methyl in each of the two methoxy-groups; thus:—



The sulphate of this base is stable, and does not appear to undergo decomposition even on long standing. In the presence of a trace of alkali, decomposition sets in at once owing no doubt to oxidation—a dark, blackish-violet solution being formed. An aqueous solution of the sulphate shows the following reactions:—

*Chlorine-water* gives a dark-violet, flocculent precipitate. *Nitric acid* gives a magnificent violet coloration which on standing—and particularly on warming—becomes a deep, reddish-brown. Berberoline solutions decompose solutions of platinic chloride, auric chloride, and ammoniacal nitrate of silver with separation of the metal.

#### *Fusion of Berberine with Potash.*

Hlasiwetz and Gilm (*Jahresbericht*, 1864, 407), who were the first to study the action of melted potash on berberine, obtained by this decomposition two new substances, that is, berberinic acid,  $C_8H_5O_4 + H_2O$ , and an acid of the formula  $C_9H_5O_5$ . With the object of determining the constitution of these two acids, I have again taken up the study of this important decomposition, the experiment being conducted as follows:—

100 grams of caustic potash and 5 c.c. of water were heated in a silver dish to about  $180^\circ$  and then 60 grams of berberine slowly added in small portions at a time. The berberine on coming in contact with the melted potash was rapidly decomposed—little black balls being formed at first, which swam about on the surface of the liquid, but on stirring, as the temperature gradually rose (to  $240^\circ$ ), these dissolved, forming a dark-brown liquid. During the operation—which lasts about an hour—a quantity of thick vapours, smelling strongly of ammonia and guaiacol, were evolved. The pro-

duct was dissolved in water, acidified with dilute sulphuric acid, filtered from a quantity of brownish flocks which separated, evaporated to a syrupy consistence, and well agitated with about twice its volume of strong alcohol. The potassic sulphate thus precipitated was filtered off, washed with a little alcohol, the combined alcoholic solutions gently evaporated on a water-bath, and the residue, dissolved in a little water, was repeatedly extracted with ether. The ethereal extract after carefully drying over calcic chloride and evaporating deposited 5 grams of a dark-brownish, crystalline mass consisting of impure berberinic acid. This was purified first by spreading it on a porous plate and then by repeated recrystallisation from water. The beautiful white crystals thus obtained gave on analysis the following numbers:—

- I. 0.1506 gram substance dried at  $80^{\circ}$  gave 0.0667 gram  $H_2O$  and 0.3160 gram  $CO_2$ .  
 II. 0.1683 gram substance dried at  $80^{\circ}$  gave 0.0735 gram  $H_2O$  and 0.3521 gram  $CO_2$ .

	Theory. $C_8H_8O_4$ .	Found.	
		I.	II.
C .....	57.15 p. c.	57.22	57.05 p. c.
H .....	4.76 „	4.92	4.84 „
O .....	38.04 „	37.86	38.11 „

Berberinic acid appears to crystallise with 1 mol.  $H_2O$ , which, however, is gradually given off at the ordinary temperatures if the crystals are placed over sulphuric acid in a vacuum. The melting point of this acid, which is not given by Hlasiwetz and Gilm, I found to be about  $165^{\circ}$ . No accurate melting point can be given, as when heated the substance softens at  $145^{\circ}$ , and then melts with evolution of carbonic anhydride at about  $165^{\circ}$ ; this temperature may therefore be looked upon as its decomposing point rather than its melting point.

The other properties of this acid agree in all respects with those given by Hlasiwetz and Gilm.

If a drop of ferric chloride is added to an aqueous solution of berberinic acid, a splendid dark-green coloration is produced which, on the addition of sodic carbonate solution, becomes first violet, then violet-red, and at last deep-red coloured. This reaction, and the fact that this acid reduces Fehling's solution and an ammoniacal solution of silver nitrate, and gives with acetate of lead a white precipitate soluble in acetic acid, shows at once that berberinic acid must be very closely related to protocathechuic acid.

As protocathechuic acid on distillation is split up into pyrocatechol and carbonic acid, it was thought that, under similar treatment,

berberinic acid might give some decomposition-product which would afford some clue as to its constitution. In order to test this, 2 grams of the pure dry acid were heated in a small retort until the evolution of carbonic anhydride had ceased, and the residue then rapidly distilled. In this way an almost colourless syrup was obtained, which on analysis gave the following numbers:—

0.1460 gram substance gave 0.0842 gram  $\text{H}_2\text{O}$  and 0.3605 gram  $\text{CO}_2$ .

	Theory. $\text{C}_7\text{H}_8\text{O}_2$ .	Found.
C .....	67.74 per cent.	67.37 per cent.
H .....	6.46 „	6.41 „
O .....	25.80 „	26.22 „

This substance has, therefore, the same formula as homopyrocatechol, with which it agrees in all its reactions. It is readily soluble in water; the solution reduces Fehling's solution and ammoniacal nitrate of silver. Ferric chloride produces a deep-green coloration which, on the addition of sodic carbonate, becomes reddish-violet. There can, therefore, be no doubt that berberinic acid on distillation is split up into homopyrocatechuic and carbonic acid, thus:—



but it is at present difficult to decide the positions of the carboxyl-group with reference to the OH and  $\text{CH}_3$ -groups.

I am at present engaged on the further investigation of oxidising agents on berberine and on the alkyl addition-products of tetrahydroberberine, and also on a series of experiments on the constitution of berberonic acid.

The completion of these experiments will be somewhat delayed owing to an unfortunate fire in the laboratories of the Heriot Watt College having consumed a number of new products which had already been prepared. For this reason also I have not been able to complete the examination of the substances described in this paper so thoroughly as I could have wished.

I hope, however, at an early date to be able to communicate to the Society a further paper on this interesting alkaloid.

*Heriot Watt College,  
Chemical Laboratory, Edinburgh.*

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XIII.—*On some Leadhills Minerals.*

By NORMAN COLLIE, Ph.D., F.R.S.E.

THE Leadhills in the south of Scotland has long been known as a locality from which many interesting minerals can be obtained. Some seemingly are peculiar to the Leadhills district, viz., *susanite*, a double sulphate and carbonate of lead; and *caledonite*, a basic sulphate of lead containing copper and carbonic acid; whilst others, viz., *leadhillite*, a mineral similar in composition to *susanite*; *lanarkite*, a basic sulphate of lead; *vanadinite* and *plumbo-calcite* are met with only in one or two other localities.

Most of the minerals, the analyses of which are given in this paper, I obtained myself some years ago at Leadhills, the remainder\* were collected by Dr. Wilson, of Wanlockhead, Leadhills. These I have from time to time analysed, with results which I have now collected in the following paper. I have also incorporated several analyses made by Mr. Wheeler, at the Queen's College, Belfast. Two minerals amongst those which I have analysed do not seem to have been previously noticed.

- (1.) *Plumbo-aragonite*, or aragonite containing lead carbonate.
- (2.) *Calcium vanado-pyromorphite*, or pyromorphite containing calcium and vanadic acid, with a small quantity of copper hydroxide.

The investigation of these Leadhills minerals was undertaken for several reasons, the chief being to ascertain whether in the large number of double carbonates, sulphates, phosphates, &c., found there, the constituent salts were present in any simple molecular proportion; another being to determine which analyses amongst the conflicting ones met with in mineralogical treatises are the most probably correct.

*Leadhillite.*

This substance is not often found at Leadhills, and for several years past, few new specimens have been obtained. It occurs also as maxite in Sardinia. The earlier analyses given differ considerably from the later ones. At one time it was considered to be a mixture of sulphate and carbonate of lead in the proportions  $\text{PbCO}_3, 3\text{PbSO}_4$ . This, however, is obviously incorrect, for not only does the substance contain from 1 to 2 per cent. of water, but there is an insufficient

\* These minerals were first given to Professor Letts of Belfast, who afterwards kindly handed them over to me for analysis.

amount of sulphuric and carbonic acids to combine with the whole of the oxide of lead. If the earlier analyses are omitted, the carbonic acid is found to vary from 8·5—12·1 per cent., as the following analyses will show :—

	I.	II.	Calculated for $4\text{PbSO}_4, 2\text{PbCO}_3, \text{Pb}(\text{OH})_2$ .
PbO.....	80·7	80·8	80·7
CO <sub>2</sub> .....	12·1	9·2	9·1
SO <sub>3</sub> .....	7·1	8·2	8·3
H <sub>2</sub> O.....	—	2·0	1·8

No. I is an analysis by Bertrand (*Bull. Soc. Chim.*, Paris, 1873).

No. II is by Hintze (*Pogg. Ann.*, 152, 256).

Three separate specimens of leadhillite were analysed, and it was found that the amount of carbonic and sulphuric acids varied considerably.

	I.			II.	III.
	(a.)	(b.)	(c.)		
PbO.....	82·5	82·3	82·1	81·8	81·3
CO <sub>2</sub> .....	8·6	8·5	8·7	9·8	11·5
SO <sub>3</sub> .....	9·1	9·2	9·2	8·0	7·3
H <sub>2</sub> O.....	1·5	1·6	1·5	1·6	1·8

These results seem to point to the fact that leadhillite varies in composition, the ratio between the sulphate and carbonate of lead not remaining constant.

#### *Lanarkite.*

This mineral is stated by Brooke and Thomson to be a compound having the formula  $\text{PbSO}_4, \text{PbCO}_3$ ; but subsequent analyses by Pisani and by Flight show that it does not contain carbonic acid, and this is corroborated by the following analyses III (a) and (b).

	I.	II.	III.		Calculated for $\text{PbSO}_4, \text{PbO}$ .
			(a.)	(b.)	
PbSO <sub>4</sub> .....	57·2	57·7	57·8	57·5	57·6
PbO .....	40·6	42·9	41·4	41·8	42·4
Loss on ignition	0·81	—	0·5	0·5	—

No. I, Pisani (*Compt. rend.*, 1873).

No. II, Flight (this Journal, 1874, 103).

Lanarkite, therefore, unlike leadhillite, seems to be of constant composition.

#### *Caledonite.*

Caledonite is one of the rarest of the Leadhills minerals, and is not



often met with. The few analyses given of it differ very considerably, the earlier ones of Brooke and Thomson giving 31·9—32·8 per cent. of lead carbonate, while Maskelyne and Flight (this Journal, 1874, 101) find only traces of carbonic acid.

	Flight and Maskelyne.		Found. Mean of two analyses.
	I.	II.	
PbSO <sub>4</sub> .....	60·2	59·5	59·1
PbO .....	25·1	26·2	24·2
CuO.....	9·4	9·2	10·7
CO <sub>2</sub> .....	1·4	—	1·9
H <sub>2</sub> O.....	—	3·7	3·5

These percentages do not agree with any simple formula, and caledonite may be a hydrated form of lanarkite, in which the hydrate of lead has been replaced by a variable amount of copper hydrate.

#### *Linarite.*

This magnificent mineral is met with at Leadhills, but fine specimens also occur in Cumberland and elsewhere. It does not seem ever to contain carbonic acid, and the analyses agree well with the formula PbSO<sub>4</sub>,CuO,H<sub>2</sub>O.

	I.	II.	Found. Mean of two analyses.	Calculated for PbSO <sub>4</sub> ,CuO,H <sub>2</sub> O.
PbSO <sub>4</sub> ..	75·4	74·8	75·3	75·6
CuO....	18·0	19·7	19·6	19·8
H <sub>2</sub> O....	4·7	5·5	5·2	4·5

#### *Pyromorphite.*

The specimens of this mineral which are found at Leadhills are remarkable for their great beauty of colour, which varies from the richest orange to light or dark olive-green. The brilliant orange variety has been supposed to contain chromium, and is sometimes called chromophosphate of lead, but there are no analyses of any pyromorphite from Leadhills containing even a trace of that metal. Another variety of pyromorphite often found is light green in colour, and in botryoidal masses with a conchoidal fracture; this seems peculiar to Leadhills, and might possibly be mistaken for calamine.

Various differently coloured pyromorphites were analysed :—

	Orange.	Green.	Yellow.	Calculated for 3Pb <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,PbCl <sub>2</sub> .
PbO.....	81·4	—	81·6	81·7
P <sub>2</sub> O <sub>5</sub> .....	15·7	15·9	15·9	15·6
Cl <sub>2</sub> .....	2·6	2·6	2·8	2·6

Arsenic acid was only present in extremely small quantity. Several experiments were also made to determine whether the green colour was due to an appreciable amount of a ferrous salt, but without success; traces of iron were present, but always seemed to be in the ferric state. From the above analyses, the pyromorphites seem to differ but little in composition.

### *Vanadinite.*

Although this mineral contains the rare element vanadium, still it has been found in various other localities besides Leadhills. It is seldom found at Leadhills in the crystalline condition, usually occurring as a deposit on calamine in the form of small granules. Two different specimens were analysed:—

	I.	II.	Calculated for $3\text{Pb}_3(\text{VO}_4)_2, \text{PbCl}_2$ .
PbO .....	80.0	79.6	78.2
$\text{V}_2\text{O}_5$ .....	16.7	16.2	19.3
Cl .....	2.5	2.4	2.5
$\text{H}_2\text{O}$ .....	1.2	1.4	—

Various specimens were tested for phosphoric acid and also for chromium, but neither of these substances was present.

### *Calcium Vanado-pyromorphite.*

This new mineral occurs in black botryoidal masses, and is unlike either pyromorphite or vanadinite in appearance. The fracture is uneven or conchoidal; it fuses easily before the blowpipe, leaving a brown granule, which when broken shows a crystalline structure. It dissolves readily in hydrochloric acid when warm, and leaves a slight residue of a brown colour, which consists chiefly of an oxide of iron. Two analyses were made:—

	I.	II.	Ratios between the phosphates, vanadates, and the lead chloride in analysis No. I.
$\text{Pb}_3(\text{PO}_4)_2$ .....	52.0	—	0.0641
$\text{Pb}_3(\text{VO}_4)_2$ .....	19.2	—	0.0224
$\text{Ca}_3(\text{PO}_4)_2$ .....	15.8	—	0.0510
$\text{PbCl}_2$ .....	11.4	10.7	0.0410
$\text{Cu}(\text{OH})_2$ .....	1.6	1.4	
Insoluble residue ..	0.6	0.5	
The specific gravity is 6.9—7.0.			

The mineral is therefore a pyromorphite in which calcium replaces

lead, and vanadic acid replaces phosphoric acid. The amount of water (0.4 per cent.) which the mineral loses when it is heated is just enough to combine with the oxide of copper, and as there is an insufficient amount of acid to unite with all the bases present, this is rendered probable. Unfortunately there was only a very small quantity of the mineral, so no further analyses could be made.

*Plumbo-calcite.*

Most of the calcite which is found at Leadhills contains some lead carbonate. The transparent crystals contain the least, whilst the opaque and vitreous looking varieties contain sometimes as much as 9.5 per cent. The specific gravity does not vary much (2.7—2.8). Six different specimens were analysed, two determinations of lead being made in each case:—

	I.	II.	III.	IV.	V.	VI.
PbCO <sub>3</sub> . . . . .	1.4	1.2	1.4	3.9	5.2	3.9
CaCO <sub>3</sub> (by diff.) . .	98.5	98.7	98.5	96.0	94.7	96.0

Lacroix (*Jahrb. f. Min.*, 1887, Ref., i, 238—239) also found that in five different specimens of plumbo-calcite from Leadhills the lead carbonate varied from 2.7 to 9.5 per cent. This mineral is evidently a varying mixture of the two carbonates.

*Plumbo-aragonite.*

It is somewhat remarkable that corussite, which is isomorphous with aragonite, should be found combined with the calcspar in plumbo-calcite, and that plumbo-aragonite should be seldom met with. That lead carbonate does, however, replace calcium carbonate in aragonite is shown by the following analyses of two undoubted specimens of aragonite from Leadhills:—

	I.	II.
PbCO <sub>3</sub> . . . . .	0.8	1.3
CaCO <sub>3</sub> (by diff.) . . . . .	99.1	98.6

Professor Heddle (*Min. Mag.*, 5, 1—31) has analysed a specimen of aragonite from Leadhills, but did not find any lead in it. CaCO<sub>3</sub> = 96.4, SrCO<sub>3</sub> = 1.7, K<sub>2</sub>O = 0.6, Na<sub>2</sub>O = 1.1, H<sub>2</sub>O = 0.3.

The specific gravity of plumbo-aragonite does not differ from that of ordinary aragonite, and is 2.9.

*Strontianite.*

Strontianite is found occasionally at Leadhills in solid, crystalline

masses of a brown colour. It contains a certain quantity of calcium carbonate. Two analyses have been made:—

	I.	II.
S <sub>2</sub> O.....	62·1	65·2
CaO .....	6·4	3·6
CO <sub>2</sub> .....	31·2	30·8

I. This analysis was made by Mr. Wheeler.

### *Dolomite.*

This dolomite is found often in very fine crystals, and has a pink colour due to oxides of iron and manganese:—

	I.	II.
CaO .....	31·2	30·6
MgO.....	14·3	14·5
FeO .....	6·1	5·3
Fe <sub>2</sub> O <sub>3</sub> .....	3·5	4·5
Mn <sub>3</sub> O <sub>4</sub> .....	0·9	0·8
CO <sub>2</sub> .....	43·3	42·6
SiO <sub>2</sub> .....	0·72	1·9

I. This analysis was made by Mr. Wheeler.

### *Calamine.*

Calamine occurs in considerable quantity at Leadhills, and can be obtained either crystalline or in botryoidal masses coloured by oxides of iron or copper:—

	Yellow.		Blue.	
	I.	II.	I.	II.
ZnO .....	59·0	59·9	60·6	62·1
SiO <sub>2</sub> .....	31·5	32·1	24·2	24·3
PbO .....	—	1·5	2·7	1·9
Fe <sub>2</sub> O <sub>3</sub> .....	1·9	—	1·9	1·2
CuO .....	—	—	trace	0·9
S .....	2·6	trace	—	—
H <sub>2</sub> O .....	4·9	5·2	10·17	9·3

The analyses marked I were made by Mr. Wheeler.

# XIV.—CONTRIBUTIONS FROM THE LABORATORY OF THE UNIVERSITY OF ZURICH.

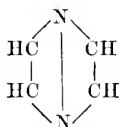
## II. *Piazine-derivatives.*

By ARTHUR T. MASON, Ph.D., F.I.C., Senior Demonstrator of  
Practical Chemistry.

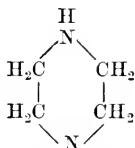
IN a paper published in the *Berichte* (20, 267), entitled "Ueber Condensations-derivate des Aethylendiamins," I described, amongst others, two substances belonging to a class of nitrogenous compounds to which, at the suggestion of Professor Merz, I gave the name "pyrazines;" this has since been changed to "piazines."\* The

\* In a paper which has just appeared in the *Journal für praktische Chemie* (38, 185), Professor Widman discusses the defective nomenclature at present adopted in the aromatic, and more especially in the alkaloïd series. In many cases, the names have been chosen so as to indicate as far as possible the methods of preparation first discovered, and then subsequent investigators, seeing the inappropriateness of the terms thus given, have adopted new ones, so that in not a few cases we have one and the same compound referred to by different investigators under totally different names. A good illustration of this is offered in the many changes which the important nitrogenous compound, above mentioned under the name of "piazine," has undergone. Its tetramethyl-derivative was discovered in 1879 by Gutknecht in V. Meyer's laboratory (*Ber.*, 12, 2290), and several other derivatives were immediately afterwards studied by Treadwell and by Treadwell and Steiger (*Ber.*, 14, 1461; 15, 1059), and named at the suggestion of Victor Meyer "ketines." At the suggestion of Professor Merz I afterwards proposed the name "pyrazines" (*Ber.*, 20, 267), and in the same Journal, Wolff adopted independently the same term (*Ber.*, 20, 425) in both instances, with the object of bringing out the analogy with the "pyridines." Victor Meyer, finding the term "ketines" inappropriate afterwards, and objecting to "pyrazines" on the ground that Knorr (*Annalen*, 238, 144) had already used that term for pyrazole tetrahydride, now proposed "aldines" (*Ber.*, 21, 20), but most of the investigators who have worked on this group still adopt the name "pyrazines." This single instance shows that a state of chaos exists, and that some systematic nomenclature is an absolute necessity. In accordance with this, Widman has propounded a systematic nomenclature for all compounds containing nitrogen in the ring. Every compound is an "azine" which contains a ring consisting of six atoms of carbon and nitrogen. He calls them respectively monazines, diazines, triazines, &c., according as they contain one or more atoms of nitrogen. To the "monazines" we should strictly have to reckon pyridine and quinoline, but to alter existing names in these cases is impracticable and unnecessary. The "diazines" are divided into three great classes, according as they contain the nitrogen-atoms in para-, meta-, or ortho-position relatively to each other. The first member of the para-class would thus be styled "paradiazine," but as this is rather long, "piazine" can be used. In the meta-class we should have "metadiazine," which when shortened gives

simplest compounds and types of this class are the hypothetical "piazine" and its hexahydride, the latter of which has long been known as "diethylenediamine."



Piazine (Pyrazine).



Piazine hexahydride or  
diethylenediamine.

The derivatives described in the above-mentioned paper were "phenanthropiazine (xenylene-pyrazine) dihydride" and "diphenylpiazine dihydride," and they were prepared by the action of ethylenediamine on phenanthraquinone and benzil respectively; but in spite of their apparently similar modes of formation, I found them to possess very different degrees of stability towards acids; for whereas the phenanthra-derivative was not altered by concentrated hydrochloric acid even at a temperature of  $200^{\circ}$ , except that a salt was formed, the diphenyl-derivative was split up into its constituents even by the dilutest mineral acids. These differences, coupled with the fact (see p. 99) that diphenylpiazine dihydride gives by the loss of two atoms of hydrogen a very stable base, have led me to the conclusions, on the one hand, that the so-called phenanthropiazine dihydride is in reality only phenanthropiazine, and, on the other hand, that the distribution of affinities is a radically different one to that holding in diphenylpiazine dihydride. That the first supposition was correct was easily proved by a new series of analytical data. For analysis, the substance was recrystallised from glacial acetic acid, and dried at  $100^{\circ}$ . The following results were obtained:—

0.1432 gram gave 0.0579 gram water and 0.4385 gram carbon dioxide.

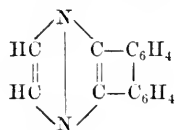
0.1540 gram gave 0.0645 gram water and 0.4694 gram carbon dioxide.

0.1500 gram gave 0.0620 gram water and 0.4605 gram carbon dioxide.

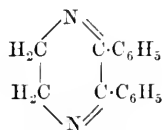
"miazine," and in the ortho-series we should have "orthodiazine," or better, "oiazine." From these three parent substances we can have derivatives containing, besides the nitrogen-ring, a benzene-ring, to denote which the syllable "phen" is prefixed. As will be seen, I have adopted Widman's nomenclature in this paper, finding it most decidedly the simplest and best.

Calculated for			Found.		
Phenanthrapiazine dihydride. $C_{16}H_{12}N_2$ .	Phenanthrapiazine. $C_{16}H_{10}N_2$ .		I.	II.	III.
C.... 82.76	83.47		83.51	83.12	83.72
H.... 5.17	4.37		4.49	4.65	4.59

These results point most decidedly to the fact that the compound is simply phenanthrapiazine, and this agrees with recent experiments made by Strache in this laboratory; he found that in the condensation of  $\alpha$ -propylenediamine with phenanthraquinone, two atoms of hydrogen also disappear, phenanthramethylpiazine being formed. The difference in the distribution of affinities in the two compounds is, I think, well expressed by the following formulæ:—

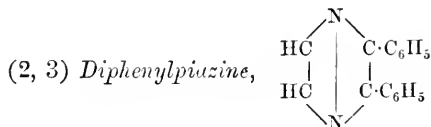


Phenanthrapiazine.



Diphenylpiazine dihydride.

In corroboration of this view I have been able to prepare from the unstable diphenylpiazine dihydride, by elimination of two atoms of hydrogen, a base which is eminently stable towards acids.



The above-mentioned dihydride melts at  $181^\circ$  to a yellow liquid, and if heated for some time about  $20^\circ$  above this temperature, the viscous mass thus obtained does not become solid and crystalline again on cooling; not until it had stood for several days were any signs of crystallisation visible. If, however, the product after two or three hours' heating at  $200^\circ$  be treated with tolerably concentrated hydrochloric acid, the greater part will dissolve on warming, and on filtering from undissolved resinous matter a solution of the hydrochloride is obtained; on adding water to this until a permanent turbidity appears, and allowing it to stand, the new base is deposited as a crystalline precipitate, the hydrochloride being decomposed by water. On recrystallisation from 50 per cent. alcohol, the substance is obtained in large, colourless plates having the melting point  $118$ — $119^\circ$ . It distils with slight decomposition at about  $340^\circ$ , small quantities of benzene and ammonia being liberated, and a car-

bonaceous residue being left. The benzene was recognised by conversion into aniline, and testing with calcium hypochlorite.

On finding that the compound was capable of distillation, I immediately tried this method of preparation, and found it decidedly the best. The dihydride is quickly distilled from a fractionating flask into a porcelain dish. It parts with two atoms of hydrogen, and the base distils as a pale-yellow oil, accompanied by a small quantity of benzene; this, however, soon evaporates, and the whole on cooling solidifies to a mass of prismatic needles which are recrystallised from amyl alcohol, and washed with cold light petroleum. The mother-liquor is freed from light petroleum and amyl alcohol by distillation, and the residue is then redistilled, when a second though small portion of base is obtained; this, however, does not crystallise until it has stood several days, and even then only partially, owing to the presence of another compound in appreciable quantity in the form of a thick, light brown syrup. The latter, on oxidation with chromic acid in glacial acetic acid solution, gave small quantities of benzoic acid, but probably no diazinecarboxylic acid; it was not further investigated. Working according to this method, and starting from 85 grams of benzil, I got 70 grams of dihydride, and from this 55 grams of crude distillate which on recrystallisation yielded 40 grams of almost pure diphenyldiazine. It is insoluble in water, easily soluble in alcohol, ether, and benzene. From light petroleum, in which it is only sparingly soluble in the cold, more easily on heating, it crystallises in beautiful, prismatic needles. The substance dried at 130° gave the following results:—

0.1833 gram gave 0.0908 gram water and 0.5595 gram carbon dioxide.

0.1620 gram gave 0.0790 gram water and 0.4929 gram carbon dioxide.

	Calculated for		Found.	
	$C_{16}H_{12}N_2$	$C_{16}H_{14}N_2$	I.	II.
C .....	82.75	82.05	83.24	82.97
H .....	5.17	5.98	5.50	5.41

Diphenyldiazine has only feeble basic properties, being precipitated by water from its solution in concentrated acids. It dissolves in concentrated sulphuric acid with a golden-yellow colour which on addition of water becomes green; if the solution in concentrated acid is heated, it gradually assumes a reddish tinge. If a crystal of potassium nitrate be added to the golden-yellow solution in concentrated acid, it immediately assumes a pale-green colour; with potassium dichromate, the colour is dirty green.



The *platinochloride*,  $(C_{16}H_{12}N_2)_3H_2PtCl_6$ , was prepared by adding hydrochloric acid to an alcoholic solution of the base, and then alcoholic platinum chloride. The salt soon separates in the form of long, yellow, prismatic needles which, as the following analyses show, are pure. The salt was dried at  $100^\circ$ .

0.1008 gram salt gave 0.0225 gram platinum.

0.1923       "       "       0.0426       "       "

	Calculated for $(C_{16}H_{12}N_2)_3H_2PtCl_6$ .	Found.	
		I.	II.
Pt .....	22.25	22.32	22.15

No methyl iodide addition product could be obtained, even on heating at  $150^\circ$ , the base behaving in this respect like the previously described phenanthrapiazine.

*Dinitrodiphenylpiazine*,  $C_{16}H_{10}N_4O_4$ , is prepared by warming a solution of the base in concentrated nitric acid for some time on the water-bath. On precipitation with water, an amorphous, yellow powder is obtained having a very low and inconstant melting point; hitherto I have not been able to obtain this substance in a crystalline form. It is easily soluble in hot alcohol, only sparingly in ether and benzene, insoluble in water and light petroleum. On rubbing the compound in an agate mortar, it becomes strongly electrical, and it is only with the greatest difficulty that it can be brought together afterwards. For analysis it was dried in a vacuum over sulphuric acid.

0.2058 gram gave 32.6 c.c. moist nitrogen at  $21^\circ$  and 730 mm.

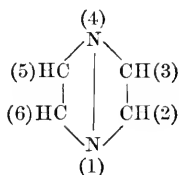
	Calculated for $C_{16}H_{10}N_4O_4$ .	Found.
N .....	17.39	17.30

#### *Reduction of Diphenylpiazine.*

The method followed was that of Wischnegradski-Ladenburg, improved by Bamberger (*Ber.*, **20**, 2915), which has yielded such excellent results of late. 15 grams of sodium were added quickly to about 50 c.c. of almost boiling amyl alcohol contained in a litre flask connected with a reflux condenser, and to this was added in a continuous stream a boiling solution of diphenylpiazine in about 200 c.c. of amyl alcohol. The solution of the base is best added by means of a long funnel hanging in the condenser tube. Immediately the first drop comes in contact with the sodium the whole assumes a rich yellow colour, and a rather violent reaction commences. The contents of the flask were kept boiling until the last particle of

sodium had disappeared, and then poured, while still hot, into about half a litre of cold water, the whole transferred to a separating funnel and well shaken in order to decompose the amyl alcoholate. The water was then drawn off, and the residue, after washing twice, was distilled from a fractionating flask till the temperature had risen to about  $150^{\circ}$  when most of the amyl alcohol had passed over. The bases, which on cooling solidify to a crystalline mass, were dissolved in dilute hydrochloric acid, filtered, and the filtrate boiled with animal charcoal till colourless. On precipitation with sodium hydrate, the bases fall as an almost white, crystalline precipitate composed of slender needles. By repeated recrystallisation from light petroleum, the mixture can be separated into two portions, from which two distinct hydrides can be isolated having the constant melting points  $122\text{--}123^{\circ}$  and  $108\text{--}109^{\circ}$ , the latter being the more easily soluble. These compounds are apparently accompanied by a third having a much lower melting point. The properties of the bases are so similar that it was only by working on considerable quantities of rather expensive material that I was able to prepare enough of the two compounds to compare their properties and those of some of their derivatives. In the following part of the paper I describe merely the experimental results hitherto obtained, reserving theoretical considerations for a future communication when I hope to have isolated the third base. The two hydrides are referred to as  $\alpha$  and  $\beta$  respectively, as on analysis they both gave numbers closely agreeing with those demanded by diphenylpiazine hexahydride.

The simplest nomenclature to adopt for the substitution products of the "piazines" is probably the one made use of in this paper; it was suggested by Knorr's nomenclature for the "pyrazoles." The following scheme will illustrate its use (*Annalen*, 238, 137):—



$\alpha$  (2, 3) *Diphenylpiazine Hexahydride*,  $\text{C}_{16}\text{H}_{18}\text{N}_2$ .

This base crystallises from light petroleum in long, slender, white needles having the constant melting point  $122\text{--}123^{\circ}$ . It is a strong base, dissolving readily in dilute acids. Analysis of the substance dried at  $100^{\circ}$  gave the following numbers:—

0.1279 gram gave 0.089 gram water and 0.3767 gram carbon dioxide.

0.1482 gram gave 0.1056 gram water and 0.4372 gram carbon dioxide.

	Calculated for $C_{16}H_{18}N_2$ .	Found.	
		I.	II.
C .....	80.66	80.32	80.66
H .....	7.57	7.73	7.91

The base is easily soluble in alcohol and benzene, less readily in ether and light petroleum, and insoluble in water.

*Hydrochloride*,  $C_{16}H_{18}N_2 \cdot 2HCl$ .—The base dissolves readily in dilute hydrochloric acid, and on evaporation and standing in the cold the salt separates in long, glistening, white needles. For analysis the salt was dried at  $100^\circ$ , a previous experiment having shown that there was no water of crystallisation in the air-dried salt. Melting point about  $310^\circ$ .

0.137 gram gave 0.126 gram silver chloride.

	Calculated for $C_{16}H_{18}N_2 \cdot 2HCl$ .	Found.
Cl .....	22.82	22.79

*Platinochloride*,  $C_{16}H_{18}N_2 \cdot H_2PtCl_6 + \frac{1}{2}H_2O$ .—The hydrochloride in aqueous solution is treated with platinic chloride; on standing, the salt separates as a yellow, crystalline powder. It is recrystallised from dilute hydrochloric acid and, as thus prepared, forms golden-yellow, prismatic needles. The analysis gave the following numbers:—

0.2499 gram of air-dried salt gave 0.0035 gram water at  $100^\circ$ .

0.2499           ,,                   ,,           0.0737   ,,   platinum.

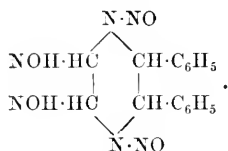
	Calculated for $C_{16}H_{18}N_2 \cdot H_2PtCl_6 + \frac{1}{2}H_2O$ .	Found.
H <sub>2</sub> O .....	1.37	1.40
Pt .....	29.61	29.49

*Nitroso-derivative*,  $C_{16}H_{16}N_6O_4$ .—The base was dissolved in dilute hydrogen chloride, and to the cold solution an aqueous solution of potassium nitrite was added as long as any precipitation took place. The white, crystalline powder was collected, washed well with water, and recrystallised from dilute alcohol. It separates after a short time in white, prismatic needles which, after a second recrystallisation, melt sharply at  $142$ – $143^\circ$  to a pale-yellow liquid. It is insoluble in water and light petroleum, easily soluble in alcohol and benzene, but only sparingly in ether. For the nitrogen determination, the substance was dried at  $100^\circ$ ; the following results were obtained:—

0.160 gram gave 33.4 c.c. moist nitrogen at  $16^\circ$  and 723 mm.

	Calculated for $C_{16}H_{16}N_6O_4$ .	Found.
N .....	23.31	23.13

The compound has, therefore, in all probability the following constitution:—



The further study of this interesting substance is reserved.

*Action of Methyl Iodide on the  $\alpha$ -Hydride,  $C_{16}H_{18}N_2$ .*

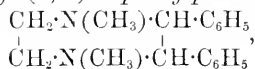
The base dissolves in methyl iodide to a clear, colourless liquid, which on warming on the water-bath to expel excess of iodide and allowing it to remain in the cold, crystallises to an almost colourless mass, the mother-liquor reacting strongly acid. Recrystallised from hot water, it forms long, colourless needles. It was dried at  $100^\circ$  for the iodine estimation:—

0.1515 gram gave 0.0889 gram silver iodide; 0.1525 gram gave 0.09077 gram silver iodide.

	Calculated for $C_{18}H_{23}N_2I$ .	Found.	
I .....	32.06	I.	II.
		31.69	32.14

It is thus seen that the substance is a hydriodide of the (1, 4) dimethyl (2, 3) diphenylpiazine tetrahydride. It is singular that only a monacid salt is formed, the other molecule of hydriodic acid remaining in the aqueous solution.

(1, 4) Dimethyl (2, 3) Diphenylpiazine Tetrahydride,



is a strong base, and is precipitated in slender, white needles from an aqueous solution of the above salt on treatment with sodium carbonate. The substance thus obtained, however, is mixed with small quantities of a compound of a very low melting point, and it is best to extract several times with ether after adding the sodium carbonate, in order to free the mixture from this product. The aqueous solution is then evaporated to a small volume, and on standing deposits the new base in long, colourless needles, having the melting point  $263-264^\circ$ . It

is easily soluble in alcohol and water on warming, but only very sparingly in ether and benzene. For analysis, the substance was dried at 100°, and the following numbers were obtained:—

0.1538 gram gave 0.1183 gram water and 0.4560 gram carbon dioxide.

	Calculated for $C_{18}H_{22}N_2$ .	Found.
C .....	81.20	80.86
H .....	8.27	8.54

*Platinum Double Salt,  $(C_{18}H_{22}N_2)_3 \cdot 2HCl \cdot (PtCl_4)_2 + 8H_2O$ .*

The base was dissolved in absolute alcohol, concentrated hydrochloric acid added, and then an alcoholic solution of platinum chloride. The salt separates as a yellowish-brown, crystalline powder, which can be recrystallised from dilute hydrochloric acid. Thus prepared the salt forms yellow, prismatic needles, which on analysis give the following numbers:—

{ 0.1496 gram air-dried salt gave 0.0127 gram water at 120°.	
{ 0.1496       "       "       "       0.0343       "       platinum.	
{ 0.1620       "       "       "       0.0130       "       water at 120°.	
{ 0.1620       "       "       "       0.0372       "       platinum.	

	Calculated for $(C_{18}H_{22}N_2)_3 \cdot 2HCl \cdot (PtCl_4)_2 + 8H_2O$ .	Found.	
		I.	II.
H <sub>2</sub> O .....	8.53	8.48	8.02
Pt .....	23.03	22.92	22.96

The salt for analyses I and II were from different preparations.

*β (2, 3) Diphenylpiazine Hexahydride,  $C_{16}H_{18}N_2$ .*

This base is more easily soluble in light petroleum than the α-compound, and remains in the filtrates together with small quantities of the base of low melting point above mentioned, from which, however, it is difficult to completely separate it. The most suitable solvent is 50 per cent. alcohol, from which it separates in long, silky, white needles. By repeated recrystallisation, the melting point ultimately becomes constant at 108–109°. When freshly prepared and still moist, the needles present a glistening, silky appearance, but on drying they become dull white, the change being in all probability due to the loss of water or alcohol of crystallisation; the distinction between the α- and β-compounds being very marked. Like the α-base, it is easily soluble in alcohol and benzene, less so in ether, and insoluble in water; it has strong basic properties, dissolving easily in dilute mineral

acids. For analysis, the substance was dried in a vacuum over sulphuric acid; the following results were obtained:—

0.1527 gram gave 0.1103 gram water and 0.449 gram carbon dioxide.  
 0.1409        „        0.099        „        „        0.4416        „        „        „  
 0.163        „        19 c.c. moist nitrogen at 25° C. and 720 mm.  
 0.1863        „        20.3        „        „        10° C.        „        723        „

	Calculated for $C_{16}H_{18}N_2$ .	Found.	
		I.	II.
C .....	80.66	80.19	80.25
H .....	7.57	8.02	7.80
N .....	11.76	12.31	12.03

*Hydrochloride*,  $C_{16}H_{18}N_2 \cdot 2HCl$ .—The base is dissolved in alcohol, concentrated hydrochloric acid added, and the whole allowed to stand, when the salt separates in colourless, prismatic needles. The melting point is about 295°. As the air-dried substance contains no water of crystallisation, it was dried at 120° for analysis:—

0.1520 gram gave 0.1384 gram silver chloride.

	Calculated for $C_{16}H_{18}N_2 \cdot 2HCl$ .	Found.
Cl .....	22.82	22.57

*Platinochloride*,  $C_{16}H_{18}N_2 \cdot H_2PtCl_6 + 2H_2O$ .—The base is dissolved in 95 per cent. alcohol, concentrated hydrochloric acid added, and then an alcoholic solution of platinic chloride. On standing, the solution deposits long, pale-yellow needles, which as the following analyses show are pure:—

0.1201 gram air-dried salt gave at 120° C. 0.0064 gram water.  
 0.1201        „        „        „        „        0.0067        „  
 0.1210        „        „        „        „        0.0339 gram platinum.

	Calculated for $C_{16}H_{18}N_2 \cdot H_2PtCl_6 + 2H_2O$ .	Found.	
		I.	II.
$H_2O$ .....	5.26	5.32	5.54
Pt .....	28.44	—	28.01

On oxidation with chromic acid in glacial acetic acid solution, (2, 3) diphenylpiazine gives a phenylpiazinecarboxylic acid, which yields well-characterised salts. The melting point is about 202°. This, as well as other products, shall be described in a future paper. In conjunction with Mr. L. A. Dryfoos, to whom I am indebted for several of the analyses in the above paper, I am studying the action of ethylenediamine on the recently discovered  $\alpha$ -diketones of the

fatty series, and have already obtained interesting results which we hope to communicate to the Society at no distant date. I cannot close this paper without expressing my thanks to Professor Victor Merz for his kindness and valuable advice during the whole of my student life at Zürich.

## XV.—CONTRIBUTIONS FROM THE LABORATORY OF THE UNIVERSITY OF ZURICH.

### No. III. *Acetamide and Phenanthraquinone.*

By ARTHUR T. MASON, Ph.D., F.I.C.

DURING experiments undertaken some time ago with the view of ascertaining whether the amido-groups in oxamide were available for condensation purposes, I had occasion to heat that substance in closed tubes with phenanthraquinone and glacial acetic acid for some hours at 220—230°. The tubes were then found to contain considerable quantities of a dark-red, crystalline substance, and on opening them a great deal of carbon monoxide and dioxide escaped. This led me to the conclusion that the oxamide, at least to a great extent, had undergone decomposition with formation of these gases, and that probably the amido-groups had reacted with the quinone. Some tubes were now filled with oxamide and glacial acetic acid alone, and heated as before for four hours to 220—230°, in order to see if at this temperature any reaction took place in the absence of phenanthraquinone.\* The whole of the oxamide had now disappeared, leaving a perfectly clear and colourless solution, and there was a great pressure on the tubes, the same gases escaping on opening as in the previous experiments. The whole was submitted to distillation from a fractionating flask. After the excess of acetic acid had gone over, the thermometer rose rapidly to about 210°, and between that temperature and 215° almost the whole distilled as a colourless liquid, solidifying in the receiver to long needles and having a slight odour of acetamide. By recrystallisation from ether or benzene, the substance entirely lost

\* The action of formic acid and acetic anhydride on oxamide was studied by Scheitz, Marsh, and Geuther in 1868 (*Zeitschrift*, 1868, 301). They state that acetic anhydride is without action on oxamide at 140—160°. This is also my experience at that temperature, but at 220—230° the reaction is complete, as shown above, even with glacial acetic acid.

the acetamide smell and was then considered to be free from that substance. On combustion of the compound, dried in a vacuum over sulphuric acid, the following results were obtained :—

0.1935 gram gave 0.1528 gram water and 0.2890 gram carbon dioxide.

0.1248 gram gave 27.5 c.c. nitrogen at 21° C. and 730 mm.

	Calculated for $C_2H_5NO$ .	Found.
C.....	40.67	40.73
H.....	8.47	8.77
N.....	23.72	24.07

These numbers, as will be seen, are the ones required by acetamide, and taking into consideration the other properties of the substance, I was forced to the conclusion that I had in reality acetamide in my hands, but freed from the smell which had hitherto been supposed to be its principal characteristic. To finally decide the point, pure acetamide obtained from Kahlbaum was redistilled and then recrystallised several times from absolute ether, whereby a perfectly odourless product was obtained, crystallising exactly like and in all respects identical with the one I had prepared from oxamide. It even suffices to rectify twice, rejecting the first portions of the distillate, which seem to contain the bulk of the odoriferous principle, in order to obtain a practically pure preparation.

Quantities of 20 grams of perfectly pure acetamide distilled completely at 213.5—214° (corr. 216.5—217° C.), with the barometer at 728 mm., and Kahlbaum's preparation twice rectified as above, distilled at exactly the same temperature.

I have since heard that results similar to those here described in connection with acetamide have been obtained in another laboratory. That my observations are the older ones, however, is clear from the fact that mention thereof was made by Professor Merz in his lectures over two years ago.

After the fact had thus been established that acetamide is one of the products of the action of acetic acid on oxamide, it was thought that this substance might also be a principal factor in the formation of the crystalline red compound mentioned above. Phenanthraquinone was therefore heated in sealed tubes with acetamide and glacial acetic acid, and, as expected, large quantities of the red, crystalline compound were obtained. It proved on investigation to be a very indifferent substance, the only solvents found being aniline, nitrobenzene, and phenol. It was repeatedly recrystallised from nitrobenzene, and ultimately obtained in the form of yellowish-brown, flat needles, having a melting point about 400°.



Great inconvenience was at first caused during its combustion, the carbon being deposited in a graphitic form on the sides of the tube and in the boat, and rendering it necessary to heat for several hours in a current of pure oxygen, before complete oxidation was effected. Working according to this method the following results were obtained on analysis. The substance for I was recrystallised from nitrobenzene five times, then washed with ether till odourless, and dried at  $120^{\circ}$ . For II, a sublimed sample was used:—

0.1692 gram	gave 0.0704 gram $H_2O$ and 0.5440 gram $CO_2$ .	
0.1330	„	0.0566 „ „ 0.4335 „
0.2045	„	13.4 c.c. moist nitrogen at $18.5^{\circ} C.$ and 728 mm.
0.2145	„	14.5 c.c. „ „ $21^{\circ}$ „ 726 „

	Calculated for $C_{28}H_{16}N_2$ .	Found.	
		I.	II.
C .....	88.42	87.68	88.88
H .....	4.21	4.62	4.72
N .....	7.36	7.21	7.33

The substance possesses, therefore, in all probability the empirical formula  $(C_{14}H_8)_2N_2$ , which is also that of a compound isolated by Sommaruga (*Jahresbericht*, 1880, 735) from the products of the action of alcoholic ammonia on phenanthraquinone, and by Japp and Burton by the distillation of ditolane-azotide over heated soda-lime. The latter authors proved that it was an azine and gave it the name tetraphenylene-azine (Japp and Wilson, *Trans.*, 1886, 830, footnote, and Japp and Burton, *ibid.*, 1887, 101). This, according to Widman's nomenclature (see previous paper), would become diphenanthrapiazine.

The compounds obtained by these different methods agree in their properties, and there can be little doubt that we have to do with one and the same substance. The yield by the above method is almost theoretical.

XVI.—*Note on Fluoride of Methyl.*

By NORMAN COLLIE, Ph.D., F.R.S.E.

IN a paper published in the *Comptes rendus* (1888, **107**, 1155), a new method is described by Moissan and Meslans for the preparation of fluoride of methyl. But as they do not seem to be aware that Dr. Lawson and myself prepared this substance by the action of heat on the fluoride of tetramethylammonium, I now take the opportunity of bringing before this Society the results of some further experiments made with this gas, although they are not yet completed. Determinations have been made of the vapour-pressures of methyl fluoride at various temperatures; the sp. gr. and critical point have also been ascertained; and the combined action of chlorine and sunlight on this gas has been studied.

The method given by Moissan for the production of methyl fluoride, namely, the action of methyl iodide on silver fluoride, is by no means so easily carried out as the one employed by Lawson and myself, for the products of the reaction have to be passed through a lead spiral cooled to  $-50^{\circ}$ , and then over silver fluoride heated to  $90^{\circ}$ , in order to free the gas from traces of iodine and methyl iodide. By the action of heat on fluoride of tetramethylammonium, a mixture of pure trimethylamine and methyl fluoride is produced, and the former can be completely absorbed by passing the vapour through a U-tube filled with pumice stone moistened with strong sulphuric acid, leaving the methyl fluoride perfectly pure.

A determination of the sp. gr. of the gas gave 17.38 as compared with hydrogen, the theoretical sp. gr. being 17.05. The following measurements of some of the physical constants of methyl fluoride were made in conjunction with Professor Ramsay. A modified Andrews apparatus, of which a drawing and description is to be found in the *Philosophical Transactions* (1887, A, p. 59), was employed. Its volume tube was filled with methyl fluoride by repeatedly exhausting and admitting the gas. The gas was then compressed and liquefied. The following table shows the vapour pressures of methyl fluoride. The pressures, it should be remarked, are absolute, the actually read pressures in the air gauges being converted by means of Amagat's measurements of the compressibility of air. The lower temperatures were secured by jacketing with water; the higher temperatures, which are more accurate, by means of alcohol vapour boiling under reduced pressures. (See Trans., 1885, **47**, 640.)

Temp.	Press.	Temp.	Press.	Temp.	Press.
	mm.		mm.		mm.
-5° C.	11365	15° C.	23003	35° C.	36204
0	14696	20	25621	40	40196
5	17740	25	28840	45	46010
10	20091	30	32756	—	—

A second series was obtained with gas presumably not so pure, inasmuch as the numbers are somewhat higher. Still the methyl fluoride must have been even then very nearly pure, as the following results at 40° show:—

	mm.		mm.
(a.) All liquid . . . . .	42962	(d.) Trace of liquid .	41951
(b.) Half gas . . . . .	41584	(e.) Smaller trace ..	41052
(c.) Liquid gone ....	39868	(f.) Minute trace ...	40622

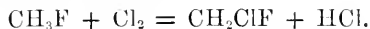
It will be observed that the last observation is nearly coincident with that of the former series at 40°. In each series, the small bubble of air was absorbed by the liquid without much rise of pressure.

The critical temperature and pressure were determined by direct observation. It need hardly be remarked that a laborious series of researches is necessary to determine the point accurately; for it can only be ascertained by constructing sets of isothermals, and deducing from them the true temperature, pressure, and volume. Still the numbers may be regarded as far more accurate than many similar determinations. The substance assumed the critical state at 44·9°, and at a pressure of 47123 mm.; here again, the pressure is probably a little too high owing to the presence of a trace of air; and the temperature too low. The error in pressure probably does not exceed 1500 mm., and the temperature 0·2°.

#### *Action of Chlorine on Methyl Fluoride.*

When chlorine and methyl fluoride are mixed in equal volumes and exposed to sunlight, substitution of the hydrogen in the methyl fluoride takes place at once, and in a few hours the mixture becomes quite colourless. Several experiments were made, and always with the same result, a chlorofluoride of methylene and hydrogen chloride was produced, and no diminution occurred in the volume of the gas; equal volumes of the two gases were formed. In one experiment, the amount of hydrogen chloride produced was titrated with decinormal ammonia solution. 128·5 c.c. of methyl fluoride were mixed with 128·5 c.c. of pure chlorine, and exposed in the sunlight for three

hours; the amount of hydrogen chloride obtained was 0.207 gram, while the amount required by theory is 0.209 gram, supposing the reaction to take place as follows:—



The methylene chlorofluoride seems to be more soluble in water than fluoride of methyl, but is easily expelled again when the aqueous solution is warmed. This property can be made use of in purifying the gas from traces of air.

The sp. gr. of the gas was found to be 3.418, while the theoretical sp. gr. is 3.425. The gas is hardly inflammable, and considerable difficulty was experienced in exploding it with oxygen alone, the combustion only taking place when a powerful electric spark was passed through the mixture; when mixed, however, with hydrogen and oxygen, it explodes easily with an ordinary electric spark.

Several analyses were made, with the following results:—

	I.	I.	III.
Taken of gas .....	4.1 c.c.	8.5 c.c.	8.5 c.c.
Carbon dioxide produced ..	4.0 „	7.5 „	8.0 „

Thus showing that the gas produced its own volume of carbon dioxide after combustion.

An estimation of the chlorine was also made; 0.03526 gram gas gave 0.072 gram  $\text{AgCl} = 50.6$  per cent.  $\text{Cl}$ .

	Found.	Calculated for $\text{CH}_2\text{ClF}$ .
$\text{Cl}$ .....	50.5	51.8

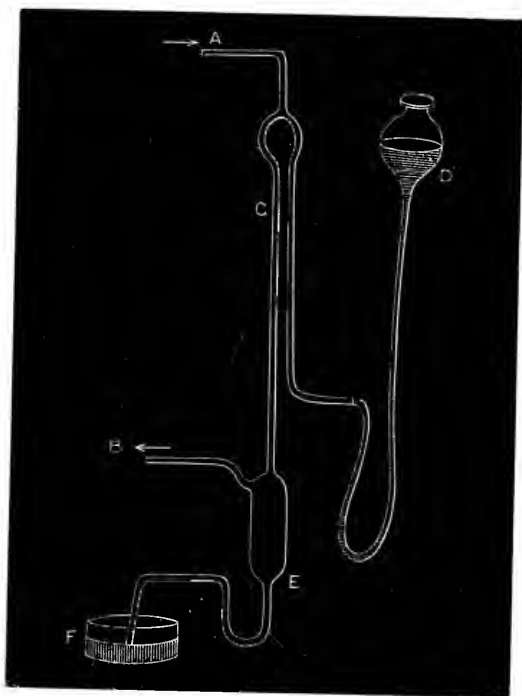
An attempt was made to estimate the fluorine, but the results were 3 per cent. too low.

Methylene chlorofluoride seems to be much more easily decomposed by water than methyl fluoride, for if an aqueous solution of this gas be allowed to stand for two or three days, both hydrochloric and hydrofluoric acids can be detected in the water.

Methylene chlorofluoride does not seem to react easily with chlorine, and the two gases when mixed in equal volumes and exposed to sunlight for many days, remain partly uncombined. I hope, however, to be able to continue the investigation.

I may mention that experiments made to obtain tetrafluoride of carbon, by passing a mixture of fluoride of silicon and carbon dioxide through a platinum tube heated to bright redness, were not successful. Silica was certainly formed in the platinum tube, and traces of a liquid were obtained which might possibly have been tetrafluoride of carbon, but unfortunately only in such small quantities that no analysis could be made.

During these experiments, when the mixture of carbon dioxide and silicon tetrafluoride was passed through a red-hot platinum tube, the following piece of apparatus was found to be extremely useful, and might doubtless be also used in many other experiments where the same result is desired. The object was to enable a continuous stream of the same gas to be slowly passed again and again through the red-hot platinum tube.



A was connected with the platinum tube, beyond which was a balloon (with two stopcocks) containing the mixed gases. B was connected directly with the balloon. The tube C was made of the ordinary glass tubing, such as is used for the Sprengel pump. When the receiver D was filled with mercury and raised just high enough to allow the mercury to flow down the tube C, gas was carried down with the falling mercury into the wider tube E; here the mercury escaped into the basin F, while the gas was forced through B back again into the balloon, and was then ready to be used again.

XVII.—*Researches on the Constitution of Azo- and Diazo-derivatives.*  
 V. *Compounds of the Naphthalene  $\beta$ -Series*—continued.

By RAPHAEL MELDOLA, F.R.S., and GILBERT T. MORGAN.

IN the last paper referring to the present branch of investigation (Trans., 1888, 460; Meldola and East), it was shown that the azo-derivatives of  $\beta$ -naphthol contain an atom of hydrogen capable of being displaced by acid radicles, a property which they share in common with their  $\alpha$ -analogues (Zincke and Bindewald, *Ber.*, 1884, 3030). Of the alkyl-derivatives of the azo- $\beta$ -naphthol compounds, the only representative at present known is the benzeneazo- $\beta$ -naphthyl ether of Weinberg (*Ber.*, 1887, 3171). The importance, from a theoretical point of view, of ascertaining whether this displaceable hydrogen-atom of the azo- $\beta$ -naphthol compounds is attached to the oxygen or to the nitrogen of the azo-group has from time to time been pointed out in the course of the present series of researches, and has recently been emphasized in a paper read by one of the authors at the Bath meeting of the British Association (*Phil. Mag.*, 1888, 403). The present paper contains the results of experiments undertaken with the object of throwing further light on this question.

I. *Benzoyl-derivatives of Azo- $\beta$ -Naphthol Compounds.*

Acetyl-derivatives of azo- $\beta$ -naphthol compounds can be prepared, as pointed out in the last paper, by two distinct methods. If the radicle attached to the azo-group is more or less of an acid character, such as nitrophenyl,  $C_6H_4 \cdot NO_2$  (*p* or *m*), the corresponding  $\beta$ -naphthylamine azo-compound is attacked by nitrous acid in the presence of glacial acetic acid, with the formation of the azo-naphthyl acetate (*loc. cit.*, p. 465).\* This method does not appear to be applicable

\* The formation of phenylic acetates from the corresponding amines, by means of the diazo-reaction in the presence of glacial acetic acid, was made known in a paper communicated to the Chemical Society of Germany on January 24th, 1888 (*Ber.*, 1888, 601), and in a subsequent paper read to this Society (Trans., May, 1888, 465), it was stated that "as the reaction promises to be widely applicable for the synthesis of phenylic acetates and other ethereal salts, it is proposed to extend the investigation in this direction, and to make a special study of the conditions which determine the displacement of amidogen by the  $C_2H_3O \cdot O$ -group by means of the diazo-reaction." Notwithstanding the publicity thus given to the method, and the explicit claim to continue its further investigation, a paper appeared in the *Amer. Chem. Jour.* of last September (10, 368) by W. R. Orndorff, containing the results of the application of this reaction for the formation of phenyl, cresyl, and

when the radicle attached to the azo-group is not acid, such as phenyl or naphthyl,  $C_6H_5$ ,  $C_{10}H_7$ , &c., in the azo- $\beta$ -naphthylamine compounds. In such cases, however, azo- $\beta$ -naphthyl acetates can be prepared by the direct acetylation of the azo- $\beta$ -naphthol compounds by means of sodium acetate and acetic anhydride, and the same method is generally applicable, whatever may be the nature of the radicle associated with the azo-group. The same remarks apply to the benzoyl-derivatives of azo- $\beta$ -naphthol compounds, some of which have been prepared by both methods in the manner described below.

*Benzeneazo- $\beta$ -Naphthyl Benzoate*,  $C_6H_5 \cdot N_2 \cdot C_{10}H_6 \cdot OC_7H_5O(\beta)$ .

This compound cannot be prepared by fusing benzeneazo- $\beta$ -naphthylamine with excess of benzoic acid, and adding the calculated quantity of sodium nitrite to the mixture: complete decomposition takes place under these circumstances with the formation of tarry products. A mixture of benzeneazo- $\beta$ -naphthol with dry sodium benzoate and benzoic anhydride, if heated for some hours to the fusing point of the anhydride, gives only a small yield of the azo- $\beta$ -naphthyl benzoate, owing to the difficulty of keeping the mixture in a homogeneous fluid condition, and to the continuous loss of anhydride by sublimation. After many partially successful attempts with benzoyl chloride, the following method was found to give perfectly satisfactory results:—

Benzeneazo- $\beta$ -naphthol is mixed with about an equal weight of dry and finely powdered sodium benzoate, and the mixture is then made just pasty with benzoyl chloride. The flask containing the mixture is fitted with a cork perforated for the reception of a tube drawn out to a fine point, and heat is applied by immersing the flask in boiling water.\* The reaction commences immediately on the application of heat, and is complete in about an hour, when the product is repeatedly extracted with hot water as long as benzoic acid is dissolved out. The contents of the flask fuse to a dark reddish oil under boiling water, a property which facilitates the washing operations, as the oil and hot water can be thoroughly mixed by agitation, and the former rapidly subsides to the bottom of the flask on allowing the contents to remain at rest for a few minutes. The benzoyl-derivative is easily decomposed by

other acetates from aniline, toluidine, &c. The investigation of the method has been going on in my laboratory since the beginning of last year, and these and other acetates and benzoates had been prepared from the diazo-salts of the corresponding amines before the appearance of the paper by the author referred to.—R. M.

\* At higher temperatures the reaction takes a different course; tarry products are formed which have not been further investigated.

ammonia, even when the latter is very dilute, so that it is unsafe to attempt to shorten the washing by the use of ammonia. In some of our first preparations, unaltered benzeneazo- $\beta$ -naphthol was always found, and this was afterwards traced to the use of ammonia in the washing waters. Sodium or ammonium carbonate also readily hydrolyse the benzoyl-derivative, and it is evident that the benzoyl-group is much more readily removed from this compound than is the acetyl from benzeneazo- $\beta$ -naphthyl acetate. When completely washed, the substance is crystallised from boiling alcohol, in which it dissolves readily. A specimen was further purified for analysis by dissolving in chloroform, in which it freely dissolves in the cold, and allowing the solvent to evaporate spontaneously in an open dish. The substance forms dense, orange-red crystals melting at  $125^{\circ}$ .

0.1025 gram gave 0.2951 gram  $\text{CO}_2$  and 0.0438 gram  $\text{H}_2\text{O}$ .

0.0894 gram burnt in a vacuum with  $\text{CuO}$  gave 5.9 c.c. moist  $\text{N}$  at  $13^{\circ}\text{C}$ ., and 770.1 mm. bar.

	Calculated for $\text{H}_{23}\text{H}_{16}\text{N}_2\text{O}_2$ .	Found.
C .....	78.41	78.52
H .....	4.55	4.74
N .....	7.95	7.90

*Metanitrobenzeneazo- $\beta$ -Naphthyl Benzoate,*  
( $m$ ) $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OC}_7\text{H}_5\text{O}(\beta)$ .

Metanitrobenzeneazo- $\beta$ -naphthylamine (m. p.  $182^{\circ}$ ) is fused with excess of benzoic acid, and the calculated quantity of dry sodium nitrite added in small portions to the fused mixture. Nitrogen is freely given off, and when all the nitrite has been added, the product is washed with hot water till free from benzoic acid. The washing may in this case be accelerated by the use of dilute ammonia without fear of decomposition. The washed product is crystallised from hot glacial acetic acid, in which it is not very soluble, and finally from boiling alcohol, in which it dissolves only very sparingly, separating on cooling in the form of dull, reddish-orange, silky needles. The melting point is  $171^{\circ}$ . The following results were obtained on analysis:—

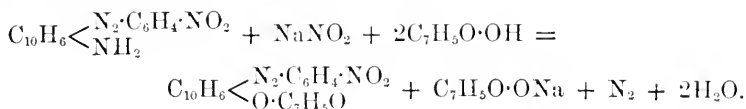
0.1676 gram gave 0.4280 gram  $\text{CO}_2$  and 0.0612 gram  $\text{H}_2\text{O}$

0.2196 gram burnt in a vacuum with  $\text{CuO}$  gave 19.8 c.c. moist  $\text{N}$  at  $17^{\circ}\text{C}$ . and 761.7 mm. bar.

	Calculated for $\text{C}_{23}\text{H}_{15}\text{N}_3\text{O}_4$ .	Found.
C .....	69.52	69.64
H .....	3.77	4.05
N .....	10.57	10.48



The substance is formed in this process according to an action perfectly similar to that which gives rise to the production of the acetate.



The benzoate may also be prepared by direct benzoylation, and this method is much more convenient when the compound is required in quantity. For this purpose, metanitrobenzeneazo- -naphthol (m. p. 194°) is mixed with about its own weight of dry powdered sodium benzoate, and enough benzoyl chloride added to make the mixture into a paste. The contents of the flask are then kept just at the boiling point of the benzoyl chloride for 4—5 hours. The product is washed with dilute ammonia, and purified by crystallisation in the manner already described.

## II. *Reduction of Azo-β-Naphthol-derivatives containing Acid Radicles.*

In order to see whether any information concerning the position of the displaceable hydrogen-atom could be derived from a study of the products of reduction of the acetyl and benzoyl-derivatives, these compounds were reduced with tin and hydrochloric acid and with stannous chloride under various conditions.

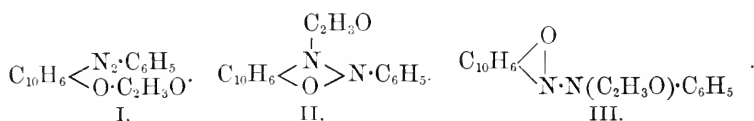
### *Reduction of Benzeneazo-β-Naphthyl Acetate.*

An alcoholic solution of the above compound is soon decolorised if boiled with tin and hydrochloric acid. On distilling off the alcohol and filtering to remove tarry impurities, the filtrate on standing gradually deposits a white curdy substance, which under the microscope is seen to consist of agglomerations of white needles. The addition of strong hydrochloric acid to the solution promotes the deposition of the white compound. The latter was therefore purified by being collected, dissolved in hot water, filtered, and reprecipitated by the addition of strong hydrochloric acid, this treatment being repeated till the substance dissolved without leaving any residue. The white substance thus obtained proved to be the hydrochloride of a mixture of bases. Many specimens were prepared and analysed without any concordant results being obtained; all attempts to separate the mixture into its constituents by fractional crystallisation or by conversion into other salts were unsuccessful. The free bases could not be isolated owing to their extremely oxidisable character. This product of reduction contains a considerable quantity of α-amido-β-naph-

thol, the presence of the latter compound being shown by the formation of  $\beta$ -naphthaquinone on oxidation by ferric chloride.

In spite of the unfavourable results obtained in our first experiments, the reduction was repeated, an alcoholic solution containing the theoretical quantity of stannous chloride being gradually mixed with a slightly warm alcoholic solution of the substance. After the mixture had stood for some hours, the alcohol was distilled off, and the product treated as above. The same white hydrochlorides were obtained, but the substance was evidently a mixture, and  $\alpha$ -amido- $\beta$ -naphthol was identified as one of its constituents as before. The analyses showed that in this case the mixture contained different proportions of the bases from those present in the product formed by violent reduction with tin and hydrochloric acid. In both series of experiments, the filtrate, after the removal of the white hydrochlorides first deposited, was treated with sulphuretted hydrogen in order to remove tin, and after the removal of the stannous sulphide the filtrate was evaporated to a small bulk, made alkaline with caustic soda, and submitted to steam distillation, when a considerable quantity of aniline was obtained, showing that this base is one of the products of reduction.

According to the current hypotheses of the constitution of the azo- $\beta$ -naphthol compounds, the acetyl-derivative of benzeneazo- $\beta$ -naphthol may have one of the following formulæ:—



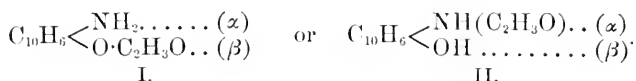
The first of these is what may be called the old formula, the second is that proposed by Liebermann, and the third is Zincke's, that is, the hydrazone formula.

Supposing the compound to be capable of complete reduction without the elimination of acetyl, these three compounds might be expected to yield the following products:—

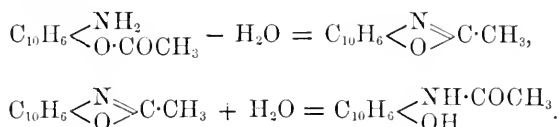
- I. Aniline and  $\alpha$ -amido- $\beta$ -naphthyl acetate.
- II. Aniline and  $\alpha$ -acetamido- $\beta$ -naphthol.
- III. Acetanilide and  $\alpha$ -amido- $\beta$ -naphthol.

We may state at once that a most careful search for acetanilide in the product of reduction has led to negative results. If the acetyl were attached to the nitrogen-atom it is improbable that this group would be removed under the conditions of reduction, since acetanilide is well known to be a stable compound under such circumstances. The third formula appears therefore to be inadmissible, and the

decision rests between Nos. I and II.\* A complication of the question, however, here arises from the possibility of intramolecular migration of the acetyl. Thus, according to the formulæ, the naphthalene portion of the molecule ought to give on complete reduction—



The investigations of Böttcher (*Ber.*, 1883, 1933) have shown that such a compound as No. I is incapable of existence, as it immediately becomes transformed into No. II. This was proved by preparing the acetyl-derivative of  $\alpha$ -nitro- $\beta$ -naphthol and reducing the latter, when a phenolic substance, viz., acetamido- $\beta$ -naphthol, was obtained instead of the basic amido- $\beta$ -naphthyl acetate. The acetyl-group accordingly becomes transferred from the oxygen to the nitrogen, probably through the intermediate formation of the anhydro-base and hydration of the latter:—



Whichever of the formulæ (I or II) be the correct one, it might therefore be expected that extreme reduction would give rise to the same acetamido- $\beta$ -naphthol. The latter is a perfectly stable phenolic substance melting, according to Böttcher, at  $225^\circ$ . It does not appear to be present, however, among the products of reduction of benzene-azo- $\beta$ -naphthyl acetate, obtained by us in accordance with the method previously described. Caustic soda does not dissolve any stable substance out of the mixed hydrochlorides, but simply gives a mixture of highly oxidisable bases, the chief constituent of which is undoubtedly  $\alpha$ -amido- $\beta$ -naphthol. The extreme reduction of the acetate therefore gives rise to the formation of aniline and  $\alpha$ -amido- $\beta$ -naphthol as chief products, a fact which is in itself of considerable importance in connection with the present line of investigation, since it shows that the acetyl-group is split off during reduction, and this lends support to the view that the said radicle is attached to oxygen, and not to nitrogen, in the original compound.

\* The formula proposed by one of the authors (Meldola, *Phil. Mag.*, Nov. 1888, p. 411) is for the present left out of consideration, because it indicates the formation of products of reduction identical with those indicated by No. I.

*Identification of  $\alpha$ -Amido- $\beta$ -Naphthol.*

At this stage of the work, seeing that the products of reduction of the acetyl-derivative contained some other base in addition to amido- $\beta$ -naphthol, it became necessary to discover a method by which the mixed bases could be converted into stable derivatives capable of being separated and characterised. The identification of the amido-naphthol itself presents but little difficulty, since it gives  $\beta$ -naphthaquinone on oxidation with ferric chloride. It is well known, however, that the formation of this quinone is somewhat capricious, and when formed it is not easy to identify, unless in a condition of tolerable purity. The quinone could not be obtained pure from our mixed hydrochlorides, because the oxidising agent also attacked the other base with which the amidonaphthol was mixed, and so gave rise to the formation of impurities of a resinous character. The method of oxidation being thus destructive to the other base, had to be abandoned. It was then found that the purified hydrochlorides when dissolved in water and treated in the cold with dilute hydrochloric acid and sodium nitrite, gave a crystalline, yellow substance which, after being collected and washed, was identified as nitroso- $\beta$ -naphthol (melting point about  $110^{\circ}$ ). This last substance is formed by the action of nitrous acid on  $\alpha$ -amido- $\beta$ -naphthol, according to a process of decomposition which has not hitherto been studied, but which has also been observed by Dr. H. E. Armstrong.\* The action of nitrous acid thus confirms the presence of  $\alpha$ -amido- $\beta$ -naphthol, but as this reagent did not appear to give a satisfactory product with the other base its use was also abandoned. Benzoyl and acetyl-derivatives of the mixed bases were next prepared, and these promised to answer our requirements, so that in the first place the benzoyl and acetyl-derivatives of pure  $\alpha$ -amido- $\beta$ -naphthol were prepared and studied, in order that we might familiarise ourselves with their properties. As these derivatives have not hitherto been described, we think it may be of use to give further particulars, as they are well characterised and stable crystalline substances, very easy of preparation, and thus offering many advantages over the quinone method for the identification of  $\alpha$ -amido- $\beta$ -naphthol, when the latter is mixed with other oxidisable bases.

Benzeneazo- $\beta$ -naphthol was reduced in alcoholic solution with tin and hydrochloric acid, the alcohol distilled off, and the amido-naphthol hydrochloride allowed to crystallise out of the solution in the usual way. This salt was collected, dissolved in water, and again crystallised with the addition of strong hydrochloric acid, this process

\* Private communication to one of the authors.

being repeated till the substance dissolved completely in water. The aniline and tin salts are thus got rid of, and the pure amidonaphthol hydrochloride is left as a white, crystalline compound. The latter was collected, drained completely from adhering mother-liquor, and dried in the water-oven. The dry salt was then just covered with glacial acetic acid, and powdered anhydrous sodium acetate and acetic anhydride added. The mixture was boiled for 2—3 hours, and the acetyl-derivative thrown out by dilution with water. The substance was collected, washed, and purified by crystallisation from alcohol, in which it readily dissolves when hot, and separates very slowly on cooling in the form of dense, colourless, transparent, rhombic prisms, melting sharply at 206°. Analysis showed that the compound was a diacetyl-derivative:—

0.1081 gram gave 0.2742 gram CO<sub>2</sub> and 0.0502 gram H<sub>2</sub>O.  
 0.1460 „ „ 7.6 c.c. moist N at 17° C. and 738.4 mm. bar.  
 0.3458 „ „ 18.2 „ „ 14.5° C. and 731.5 „

	Calculated for $C_{10}H_6 \begin{cases} NH \cdot C_2H_3O \\ O \cdot C_2H_3O \end{cases}$	Found.	
		I.	II.
C .....	69.13	69.18	—
H .....	5.35	5.16	—
N .....	5.76	5.84	5.94

The substance is accordingly acetamido- $\beta$ -naphthyl acetate. It is of interest to note that the acetylation in this case leads to the formation of a diacetyl-derivative and not of an anhydro-base, although the amidonaphthol is an ortho-derivative. As a parallel instance, we may mention  $\alpha$ - $\beta$ -naphthylenediamine which, although an ortho-compound, also gives a diacetyl-derivative, and not an anhydro-base, on acetylation (Lawson, *Luug. Diss.*, 1885, p. 26).

By heating dry amido- $\beta$ -naphthol hydrochloride with anhydrous sodium benzoate and benzoyl chloride to the boiling point of the latter, for about two hours, a dibenzoyl-derivative is formed. The product of the reaction is washed repeatedly with hot water and dilute ammonia, and finally purified by two or three crystallisations from boiling alcohol, in which the substance dissolves somewhat sparingly. The pure compound forms whitish needles melting at 226.5°.

0.1186 gram gave 0.3420 gram CO<sub>2</sub> and 0.0544 gram H<sub>2</sub>O.  
 0.1508 gram burnt in a vacuum with CuO gave 5 c.c. moist N at 24.5° and 765.3 mm. bar.

	Calculated for $C_{10}H_6 < \begin{matrix} XII \cdot C_7H_5O \\ O \cdot C_7H_5O \end{matrix}$	Found.
C .....	78.47	78.66
H .....	4.63	5.09
N .....	3.81	3.73

These results show that the compound is benzamido-3-naphthyl benzoate and that, as in the case of acetylation, both the hydroxyl and amidogen of the amidonaphthol are simultaneously attacked.

*Mild Reduction of Benzeneazo- $\beta$ -Naphthol and its Acetyl-derivative.*

In accordance with the well-known fact that aromatic azo-compounds by mild reduction yield hydrazo-compounds, which under the influence of acids become transformed into bases of the diphenyl or naphthylphenyl series, it became of interest to investigate the action of mild reducing agents on the azo-compounds of  $\beta$ -naphthol. Commencing with the simplest case, benzeneazo- $\beta$ -naphthol was dissolved in a sufficient quantity of alcohol to retain the whole of the substance in solution when cold, and stannous chloride mixed with alcohol was added to the solution till reduction had been effected. The alcohol was distilled off, and the residual solution, after filtration to remove a small quantity of tarry matter, was mixed with dilute sulphuric acid, and allowed to stand for 24 hours. A small quantity of a crystalline substance, consisting of slender, white needles, had separated, but the yield was too small to enable analyses to be made. The presence of sulphuric acid was proved qualitatively in the compound after the latter had been purified by crystallisation from boiling water, in which it dissolves with great difficulty. The substance is in all probability the sulphate of diamido-oxynaphthylphenyl, and we hope to return to its investigation on a future occasion, but the small yield has deterred us from making further experiments in this direction, as the preparation of this compound has only an indirect bearing on the present line of work. The free base is very unstable, forming dark products of oxidation with extreme rapidity on exposure to the air. During the boiling of the solution of the sulphate for the purpose of purifying this salt, a considerable loss was incurred by the formation of a resinous product. If the sulphate is basified by ammonia, a greenish colouring matter is produced by the action of atmospheric oxygen. A small quantity of the sulphate heated with dry sodium acetate and acetic anhydride gave an acetyl-derivative, which, after crystallisation from alcohol, formed small, white needles melting at 130—131°.

Benzeneazo- $\beta$ -naphthyl acetate, when reduced in a similar manner

with stannous chloride in cold alcoholic solution, gives a mixture of bases from which nothing definite could be isolated. Amido- $\beta$ -naphthol is undoubtedly present, but not in sufficient quantity to separate out as a hydrochloride in the presence of excess of acid. The presence of amido- $\beta$ -naphthol was proved by the formation of nitroso- $\beta$ -naphthol by the action of sodium nitrite on the acid solution. The other base which is present is so readily decomposable that a dark resinous scum is continually formed during the evaporation of the solution. The addition of sulphuric acid to the solution of the hydrochlorides does not cause the separation of an insoluble sulphate. Nevertheless the absence of a naphthylphenyl base cannot be inferred from this circumstance, because it is highly probable that such a base, if formed, would contain the acetyl-group in one of the amidogens, and would thus lose the property of forming an insoluble sulphate. We have proved that such a naphthylphenyl-derivative is formed by a method which is described further on, so that the unstable base present in solution with the amidonaphthol is in all probability the acetyl-derivative of diamidohydroxynaphthylphenyl with the acetyl in one of the amidogen-groups by intramolecular transference, *i.e.*,

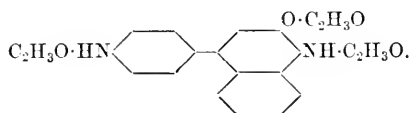


The proof that such a base is formed is furnished by the isolation of the diacetyl-derivative. The mixture of dry hydrochlorides, obtained by the reduction of benzeneazo- $\beta$ -naphthyl acetate in *slightly warm* alcoholic solution with stannous chloride, was boiled for about two hours with glacial acetic acid, dry sodium acetate, and acetic anhydride. The product was diluted with water, collected, washed, and crystallised two or three times from hot alcohol. Microscopic needles were obtained, melting sharply at  $252^\circ$ . From the first mother-liquor there slowly separated the familiar rhombic prisms of acetamido- $\beta$ -naphthyl acetate (m. p.  $206^\circ$ ). The substance melting at  $252^\circ$  was analysed with the following results:—

- I. 0.1513 gram gave 0.3892 gram  $\text{CO}_2$  and 0.0724 gram  $\text{H}_2\text{O}$ .  
 II. 0.1310           "           0.3368           "  
 III. 0.1194         "           0.3076         "           "           0.0581         "  
 IV. 0.2154        "           13.1 c.c. N at  $15^\circ$  C. and 745 mm. bar.

	Calculated for $\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}_4$ .	Found.			
		I.	II.	III.	IV.
C .....	70.21	70.15	70.12	70.26	—
H .....	5.31	5.31	—	5.40	—
N .....	7.44	—	—	—	6.98

These numbers indicate that the compound is the triacetyl-derivative of diamido-hydroxynaphthylphenyl, the constitutional formula being—



The other base mixed with the amido- $\beta$ -naphthol is, accordingly, the monacetyl-derivative of diamido-hydroxynaphthylphenyl, the acetyl being most probably present in the  $\alpha$ -amidogen-group through intramolecular migration in the manner explained. The absence of two amidogen-groups in the monacetyl-derivative appears, as we have already stated, from the fact that it does not form an insoluble sulphate, a property which is so eminently characteristic of all the bases of the benzidine series, and which, as we have previously shown, pertains to diamido-hydroxynaphthylphenyl itself.

Summing up the results given by the present investigation of the products of reduction of benzeneazo- $\beta$ -naphthyl acetate, the following conclusions have been arrived at:—

1. By violent reduction with tin and hydrochloric acid, the chief product is  $\alpha$ -amido- $\beta$ -naphthol, a small quantity of the monacetyl-derivative of diamidohydroxynaphthylphenyl being at the same time produced. The splitting off of acetyl favours the view that this radicle is attached to the oxygen atom and not to the nitrogen atom.

2. Reduction in cold alcoholic solution with stannous chloride gives monacetyldiamido-hydroxynaphthylphenyl as the chief product,  $\alpha$ -amido- $\beta$ -naphthol being at the same time formed in smaller quantity.

3. Moderate reduction with stannous chloride in warm alcoholic solution gives a mixture of the two bases, from which the triacetyl-derivative of the hydroxynaphthylphenyl base can be isolated by acetylation and crystallisation of the product.

In all three cases, aniline is also one of the products of reduction.

#### *Reduction of Benzeneazo- $\beta$ -Naphthyl Benzoate.*

When this compound is reduced by boiling its alcoholic solution with tin and hydrochloric acid, the products are aniline and  $\alpha$ -amido- $\beta$ -naphthol, the benzoyl-group being split off as in the case of the acetate when it is submitted to violent reduction. A cold alcoholic solution of the benzoate, when mixed with a solution of stannous chloride, also gives a considerable quantity of amido- $\beta$ -naphthol together with a benzoyl-derivative of a naphthylphenyl base. The



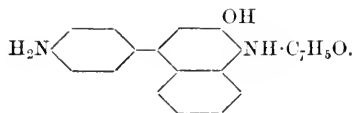
separation of the two products in this case offers no difficulty, as the basic properties of the latter are neutralised by the benzoyl-group and the substance is insoluble in dilute acids. After the reduction is complete, the alcohol is distilled off, the residue diluted with water and filtered. The filtrate contains the amido- $\beta$ -naphthol hydrochloride, which can be identified in the usual manner. The dark, tarry, insoluble residue left after this treatment is extracted two or three times with hot dilute hydrochloric acid, then washed with water, and finally extracted with cold alcohol, which dissolves out a tarry impurity and leaves the crude naphthylphenyl-derivative in the form of a whitish, crystalline powder. The latter, after being twice crystallised from boiling alcohol, in which it is rather sparingly soluble, forms white, silky needles melting at  $172$ — $173^{\circ}$  :—

0.1004 gram gave 0.2860 gram  $\text{CO}_2$  and 0.0416 gram  $\text{H}_2\text{O}$ .

0.0813 gram burnt in a vacuum with  $\text{CuO}$  gave 5.5 c.c. moist  $\text{N}$  at  $14^{\circ}$  C and 750.9 mm. bar.

	Calculated for $\text{C}_{23}\text{H}_{18}\text{N}_2\text{O}_2$ .	Found.
C .....	77.96	77.69
H .....	5.08	4.60
N .....	7.91	7.86

The formula deducible from these analyses indicates that the compound is a monobenzoyl-derivative of diamidohydroxynaphthylphenyl. The yield is not very great, as the chief products of reduction are, even under the described conditions of working, chiefly amido- $\beta$ -naphthol and aniline. The fact that the substance is not basic tells against the view that two amido-groups are present, and points to the transference of the benzoyl from the oxygen to the nitrogen in the naphthalene nucleus by the same process as that which takes place with the corresponding acetate. We are, therefore, led to the view that the constitutional formula of the compound is—



The proposed formula certainly indicates a phenolic substance, whereas our compound is insoluble in aqueous alkali. The disguising of the phenolic character of the molecule by the proximity of the  $\text{C}_7\text{H}_5\text{O}-\text{NH}$ -group seems, however, more probable than that two free amido-groups should be present when the distinctly non-basic character of the substance is borne in mind. For this reason we attach the greater weight to the above formula.

The general conclusion to which these experiments point is that the acid radicle, acetyl or benzoyl, introduced into benzeneazo- $\beta$ -naphthol or its derivatives displaces an atom of hydrogen which is attached to oxygen and not to nitrogen. This is shown by the facility with which the radicle is split off during reduction and by the absence of acetanilide or benzanilide among the products of reduction. The transference of the radicle from the oxygen to the nitrogen in the naphthylphenyl base is effected by intramolecular change in the ortho-position, through the intermediate formation of an anhydro-base. An investigation of the products of reduction of the alkyl-derivatives of azo- $\beta$ -naphthol compounds has been carried on concurrently with the foregoing experiments, and the results will be made known in a subsequent communication. In the early part of the present research, we received much assistance from Mr. E. H. R. Salmon, and more recently we have had the benefit of the co-operation of Mr. J. H. Coste. It gives us much pleasure to acknowledge the services rendered by these gentlemen.

*Finsbury Technical College.*

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#### XVIII.—*Action of Bromine and Chlorine on the Salts of Tetrethyl-phosphonium.*

By ORME MASSON, M.A., D.Sc. (Edin.), and J. B. KIRKLAND.  
University of Melbourne.

THE action of the halogens on trimethylsulphine salts formed the subject of a paper communicated to the Society by Dobbin and one of us (Trans., 1885, 56), and in a subsequent communication the action of the halogens on tetramethylammonium salts was described by the same authors (Trans., 1886, 846). In these papers, it was shown that the haloid salts of these bases can combine directly with iodine, bromine, chlorine, or iodine monochloride, to form compounds of the general formula  $RX_3$  (where R is the basic radicle and X is I, Br, or Cl); that those members of the series which contain not less than one atom of iodine in the molecule are fairly stable crystalline solids of a characteristic black, red, or yellow colour; that the other members, containing only bromine or chlorine, or both, are red or yellow liquids, stable only in an atmosphere of the halogen from which they have been formed; that some of these unstable compounds have a sufficiently definite composition (corresponding to the general formula  $RX_3$ ) as proved by synthetic experiments; but that

others have a tendency to absorb a large excess of halogen without very great alteration of properties, particularly where bromine is the halogen added. It was also shown that this formation of perhaloid compounds is an action of wider application than, at first, would seem probable; for not only may the nature of the organic basic radicles be varied very considerably, but qualitative experiments with the sulphates of trimethylsulphine and tetramethylammonium showed that these, as well as the haloid salts, can combine directly with bromine and chlorine. The striking resemblance between the behaviour, in this respect, of the sulphates and the chlorides led the authors to reject that view of the constitution of the perhaloid compounds which is represented by the formula  $R'X \leq \frac{X}{X}$ ; and the option was left of regarding them all as molecular compounds of the formula  $R'X, X_2$ , or of regarding the central atom of the basic radicle (S or N) as capable of directly attaching to itself the additional halogen atoms ( $R''X_3$ ). Quantitative data, however, were required to fully prove the similarity of the action of the sulphates and chlorides or bromides. It was thought that more stable compounds might be obtained from the salts of a phosphorus base, and a preliminary experiment with tetrethylphosphonium iodide showed that at any rate this salt is capable of yielding perhaloid compounds resembling those already studied. The investigation was then interrupted, and has only lately been resumed by the present authors. Tetrethylphosphonium salts have been used on account of the greater ease with which they may be prepared as compared with the methyl compounds. The iodide was prepared by Hofmann's method from phosphonium iodide and absolute alcohol, and was proved by analysis to be of sufficient purity.

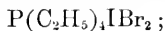
	P.	C.	H.	I.
Found (per cent.) .....	—	34.79	7.39	45.68
Calculated (per cent.).....	11.31	35.03	7.29	46.35

In any future experiments, however, we should prefer the method of preparation described by us in the next paper (p. 138), on account of its greater simplicity and economy.

*Action of Bromine on Tetrethylphosphonium Iodide.*

When bromine is added to this salt, combination occurs, accompanied by the development of much heat, the whole phenomena

being similar to those observed in the cases of the iodides of trimethylsulphine and tetramethylammonium. When the resulting heavy red liquid is freed from excess of bromine by evaporation and by washing with anhydrous ether, a bright red solid remains, which dissolves in warm alcohol, and on evaporation may be obtained in orange-red crystals. The appearance and properties of these leave no room for doubting that they are *tetrethylphosphonium dibromiodide*,



this was confirmed by analysis.

\*I. 0.1809 gram gave 0.1450 gram  $\text{CO}_2$  and 0.0880 gram  $\text{H}_2\text{O}$ ; or 0.03955 gram C and 0.00798 gram H.

II. 0.1970 gram gave, after reduction with sulphurous acid, 0.2800 gram of the mixed silver salts  $\text{AgBr}$  and  $\text{AgI}$ . Assuming this mixture to be in the proportion  $2\text{AgBr} : \text{AgI}$ , it contains 0.07332 gram Br and 0.05820 gram I.

		Found.	
Calculated for $\text{P}(\text{C}_2\text{H}_5)_4\text{IBr}_2$ .		I.	II.
P .....	7.14	—	—
C .....	22.12	21.86	—
H .....	4.61	5.40	—
I .....	29.26	—	29.54
Br .....	36.87	—	37.22
<hr/>			
100.00			

This dibromiodide, like those previously described, yields a black explosive substance when treated with aqueous ammonia; and forms an additive compound of the formula  $\text{P}(\text{C}_2\text{H}_5)_4\text{IBr}_2 + 2\text{NH}_3$ , when subjected to the action of a current of dry ammonia. This compound is black in colour. When left exposed to the air it loses ammonia, and leaves the dibromiodide as a red powder.

0.1470 gram of the dibromiodide yielded 0.1582 gram of the black ammonia compound.

\* This dibromiodide, the corresponding dichloriodide, and the tribromide, were found to present unusual difficulties when submitted to combustion—difficulties not met with in the case of tetrethylphosphonium iodide on the one hand, or of the perhaloid compounds of trimethylsulphine and tetramethylammonium on the other. An open tube was employed with oxide of copper and chromate of lead, with silver at the exit end. The combustions had to be conducted with extreme slowness to avoid loss of phosphine-smelling volatile matter (which spoilt the first experiments), and in every case a refractory black residue remained which yielded only to prolonged heating in the oxygen current. This may account for the high percentages of hydrogen found, though all the usual precautions were employed for drying the gas.

	Percentage increase of weight.
Calculated for $P(C_2H_5)_4IBr_2 + 2NH_3 \dots$	7.26
Found .....	7.47

A synthetic experiment was made in order to ascertain whether, by bromination of the iodide, any compound could be obtained containing more bromine than the dibromiodide. 0.3087 gram of the dry iodide was exposed for three-quarters of an hour at the ordinary temperature to a current of dry air laden with bromine vapour. The iodide was contained in a porcelain boat placed in a glass tube, and the boat and tube, together with the glass stopper, were tared at the commencement. After clearing out the tube with a rapid current of dry air, it was found that there was an increase of weight equivalent to a gain of 3.4 atoms of Br by each molecule of  $P(C_2H_5)_4I$ . The product was a dark-red liquid. The tube was now placed in an air-bath, and kept at  $110^\circ$  for two hours, whilst the bromine current was kept up, and the increase of weight was again ascertained, and found to be equivalent to a gain of 5.2 atoms of bromine by each molecule of  $P(C_2H_5)_4I$ , though there was not much change in the appearance of the liquid product. This was then subjected to a current of pure dry air at the ordinary temperature, and weighed from time to time. It was soon converted into a bright-red solid substance, and this continued to lose bromine slowly, but after three hours still retained what was equivalent to 3.6 atoms for each molecule of the iodide.

Bromine passed.	Dry air passed.	Weight found.	Increase per cent.	Atoms of Br per mol.	Nature of product.
$\frac{3}{4}$ hour, cold.	—	0.6172	99.9	3.4	Liquid.
2 hours at $110^\circ \dots$ }	—	0.7827	153.0	5.2	Liquid.
—	3 hours	0.6320	104.7	3.6	Solid.

Weight of iodide used, 0.3087 gram.

There is, then, a marked tendency for  $P(C_2H_5)_4I$  to take up more than  $Br_2$ , but if a definite higher compound exists, it is of an unstable nature. It will be seen that the behaviour of the iodide towards chlorine favours, by analogy, the supposition that an unstable *tetra-bromiodide*,  $P(C_2H_5)_4IBr_4$ , may exist.

*Action of Chlorine on Tetrethylphosphonium Iodide.*

The absorption of chlorine by the dry salt is attended by development of heat and the formation of a substance which, at first brown,

becomes yellow as the action proceeds; it is facilitated by keeping the salt at a temperature of about  $70^{\circ}$ , in which case a red liquid is obtained that solidifies to a darkish yellow, crystalline mass on cooling in an atmosphere of chlorine. Its composition was ascertained by the following synthetic experiment, which was conducted in a manner similar to that already described:—

Weight of iodide taken .....	1.011 gram.
Chlorine passed at $70^{\circ}$ .....	1 hour.
Weight of product (solid) .....	1.520 gram.
Percentage increase of weight.....	50.3 per cent.
Percentage increase calculated for forma- tion of $P(C_2H_5)_4ICl_4$ .....	51.8 per cent.

This *tetrachloriodide* very slowly loses chlorine in dry air, but decomposes with loss of chlorine when treated with water or alcohol.

Its alcoholic solution, on evaporation, yields yellow crystals of the *dichloriodide*,  $P(C_2H_5)_4ICl_2$ , a substance closely resembling the dichloriodides previously described, both in appearance and in its reactions with ammonia, &c. On analysis it gave the following results:—

- I. 0.1233 gram gave 0.1255 gram  $CO_2$  and 0.075 gram  $H_2O$ , equivalent to 0.03423 gram C and 0.00833 gram H.
- II. 0.1586 gram, after reduction with sulphuric acid, gave 0.2368 gram of mixed silver salts. On the assumption that this contains iodide and chloride in the proportions of  $AgI:2AgCl$ , it is equivalent to 0.0576 gram I and 0.0322 gram Cl.

	Calculated for $P(C_2H_5)_4ICl_2$ .	Found.	
		I.	II.
P .....	8.98	—	—
C .....	27.83	27.75	—
H .....	5.80	6.74	—
I .....	36.81	—	36.32
Cl .....	20.58	—	20.30
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100.00			

#### *Action of Bromine on Tetrethylphosphonium Bromide.*

The bromide employed was made from the iodide by shaking its solution with recently precipitated silver bromide. An estimation of the bromine showed it to be of sufficient purity.

	Br per cent.
Found .....	34.79
Calculated for .....	35.24

A synthetic experiment with this salt showed that when subjected to the action of bromine-vapour at  $110^{\circ}$  it absorbs it to form a dark-red liquid, which at the ordinary temperature is converted into a scarlet, crystalline solid having the composition indicated by the formula  $P(C_2H_5)_4Br_7$ , that is, the bromide is converted into the *heptabromide* by addition of six atoms of bromine. The details of the experiment are given in the following table:—

Weight of bromide taken .....	0.1472 gram.
Bromine current at $110^{\circ}$ .....	1 hour.
Weight of product (solid) .....	0.4554 gram.
Increase of weight .....	209.4 per cent.
Increase calculated for $P(C_2H_5)_4Br_7$ .....	211.4 per cent.

This heptabromide, like the higher compounds derived from the iodide, is not stable in air and also loses part of its bromine when treated with absolute alcohol. The alcoholic solution yields red crystals of the *tribromide*,  $P(C_2H_5)_4Br_3$ . This compound closely resembles the dibromiodide, but does not form an addition product with ammonia and is dissolved by ammonia solution. No solid tribromides were obtained from trimethylsulphine or tetramethylammonium, but only unstable red liquids. The difference in behaviour in the present instance may be wholly attributable to the presence of ethyl in place of methyl radicles, rather than to the presence of phosphorus in place of sulphur or nitrogen; for Marquardt (*J. pr. Chem.* **1**, 429) obtained a solid tribromide of tetrethylammonium. The following were the results obtained by analysis:—

- I. 0.2046 gram gave 0.1860 gram  $CO_2$  and 0.1022 gram  $H_2O$ , equivalent to 0.05073 gram C and 0.01135 gram H.
- II. 0.2645 gram gave 0.2380 gram  $CO_2$  and 0.1362 gram  $H_2O$ , equivalent to 0.06491 gram C and 0.01513 gram H.
- III. 0.1808 gram, after reduction with sulphuric acid, gave 0.2040 gram AgBr, equivalent to 0.11234 gram Br.

	Calculated for $P(C_2H_5)_4Br_3$ .	Found.		
		I.	II.	III.
P .....	8.01	—	—	—
C .....	24.80	24.79	24.54	—
H .....	5.18	5.54	5.72	—
Br .....	62.01	—	—	62.14
<hr/>				
100.00				

*Action of Chlorine on Tetrethylphosphonium Chloride.*

The chloride employed was prepared by shaking a solution of the iodide with recently precipitated silver chloride, and was thoroughly dried by heating in a current of dry air at  $110^{\circ}$ . The salt absorbs chlorine and turns yellow at the ordinary temperature, but the action goes better at  $105\text{--}110^{\circ}$ . Under these conditions, a yellow liquid is obtained which, on cooling, solidifies to a yellow, crystalline mass. A quantitative experiment showed this to consist of the *trichloride*,  $\text{P}(\text{C}_2\text{H}_5)_4\text{Cl}_3$ .

Weight of chloride taken.....	0.1172 gram.
Chlorine passed in the cold.....	$2\frac{1}{2}$ hours.
Chlorine passed at $105\text{--}110^{\circ}$ .....	$1\frac{1}{2}$ „
Weight of product (solid).....	0.1608 gram.
Increase of weight.....	37.2 per cent.
Calculated increase for $\text{P}(\text{C}_2\text{H}_5)_4\text{Cl}\cdot\text{Cl}_2$	38.9 per cent.

The trichloride is a yellow, crystalline substance which deliquesces in the air and is decomposed by water and alcohol with reformation of the chloride. Like other perhaloid compounds it is insoluble in anhydrous ether. There appears to be no tendency to form a higher addition product than the trichloride.

*Action of Bromine on Tetrethylphosphonium Sulphate.*

The sulphate was prepared from the iodide by means of silver sulphate. In order to thoroughly dry the salt obtained by evaporation of the solution, it was found necessary to heat it for some hours at a temperature ranging from  $100^{\circ}$  to  $170^{\circ}$  in a Sprengel vacuum. It was then submitted to the action of bromine vapour in the same manner as the bromide, the increase of weight being observed first after bromination at  $110^{\circ}$ , and subsequently after further bromination at the ordinary temperature. It was found that the sulphate has the power of taking up a large quantity of bromine, but that the amount absorbed and the character of the product vary considerably according to the temperature. The product formed at  $110^{\circ}$  is, when cold, a red solid; and the increase of weight in this case corresponds to the formation of  $[\text{P}(\text{C}_2\text{H}_5)_4]_2\text{SO}_4\text{Br}_{12}$ ; and this, it may be remarked, is analogous to the highest brominated derivative of the bromide,  $\text{P}(\text{C}_2\text{H}_5)_4\text{Br}\cdot\text{Br}_6$ , which it closely resembles in its general properties—appearance, instability in air, decomposition by alcohol, &c. The product formed at the ordinary temperature differs from this, being a dark red liquid and containing a still larger amount of bromine. In the two experiments made, details of which are given below, the



increase of weight at the ordinary temperature corresponded closely with that required for the formation of  $[\text{P}(\text{C}_2\text{H}_5)_4]_2\text{SO}_4\text{Br}_{22}$ ; but it is doubtful whether this really marks the formation of a distinct compound or the extreme limit of bromine absorption. When this highly brominated liquid is left in a desiccator over solid potash, or when it is treated with a current of dry air, it quickly loses bromine and assumes the solid state; but the decomposition does not stop here, and we have not succeeded in obtaining any brominated sulphate of stability equal to that of the tribromide or the dibromiodide.

Experiment.	I.	II.
Weight of sulphate used, in grams ..	0.2678	0.2192
Bromine passed at 110° .....	1 hour	1 hour
Weight of product (solid) .....	0.9206	0.7552
Percentage gain of weight .....	243.8	244.5
Bromine subsequently passed in cold..	2 hours	1 hour
Weight of product (liquid) .....	1.4848	1.2207
Percentage gain of weight .....	454.4	456.9
Percentage gain calculated for $[\text{P}(\text{C}_2\text{H}_5)_4]_2\text{SO}_4\text{Br}_{22}$	451.3	
Percentage gain calculated for $[\text{P}(\text{C}_2\text{H}_5)_4]_2\text{SO}_4\text{Br}_{12}$	246.2	

The solid brominated sulphate dissolves in alcohol and red crystals are formed in quantity when the solution is partly evaporated; but a study of these and estimations of the bromine proved them to consist of tetrethylphosphonium tribromide. It was proved that the crystals contained no sulphuric acid, but the mother-liquor was found to be strongly acid. The alcohol, therefore, produces decomposition, and it is interesting to note that the phosphorus radicle retains the bromine in preference to the sulphuric acid group.

I. 0.1196 gram, after reduction with sulphurous acid, gave 0.176 gram AgBr, equivalent to 0.07489 gram Br.

II. 0.0492 gram gave 0.072 gram AgBr, equivalent to 0.03064 gram Br.

	Calculated for for $\text{P}(\text{C}_2\text{H}_5)_4\text{Br}_3$ .	Found.	
		I.	II.
Br per cent.....	62.01	62.62	62.27

#### *Action of Chlorine on Tetrethylphosphonium Sulphate.*

The thoroughly dried sulphate combines with chlorine, but less readily and (as in other cases) to a less extent than with bromine. The salt turns yellow, and, if the temperature be raised to 130° while the chlorine is passing, fuses to a yellow liquid, which solidifies on cooling in the chlorine atmosphere. In the two experiments made, it

was found that the increase of weight corresponded to the formation of the compound  $[P(C_2H_5)_4]_2SO_4Cl_4$ ; and this, it may be noted, is analogous to the formation of the chlorinated chloride  $P(C_2H_5)_4Cl, Cl_2$ , already described. The sulphate, therefore, appears to resemble the bromide in its action towards bromine and the chloride in its action towards chlorine, both as to the composition and as to the appearance and properties of the products formed. This is in accordance with the previously recorded qualitative observations on the sulphates of trimethylsulphine and tetramethylammonium.

Experiment.	I.	II.
Weight of sulphate used, in grams....	0.2172	0.2018
Chlorine passed at 130°.....	1½ hours	1½ hours
Weight of product.....	0.2964	0.2790
Percentage gain of weight .....	36.4	32.2
Percentage gain calculated for $[P(C_2H_5)_4]_2SO_4Cl_4$	36.4	

This chlorinated sulphate dissolves in water with effervescence, due to escape of chlorine, deliquesces when exposed to the atmosphere, and slowly evolves chlorine when subjected to a current of dry air.

The following table contains a list of the polyhaloid-derivatives described in this paper, together with a summary of the methods of forming them and of their properties. In some cases the formulæ given are doubtfully indicative of definite compounds.

No.	Compound formed.	Method of formation.	Temp. of formation.	Characters of the compound.
1..	$P(C_2H_5)_4IBr_4$ (?) .....	Bromine on iodide.	cold	Bright red cryst. solid, unstable in air.
2..	$P(C_2H_5)_4IBr_2$ .....	Alcohol on 1.....	—	Orange crystals: stable.
3..	$P(C_2H_5)_4ICl_4$ .....	Chlorine on iodide.	70°	Dark yellow cryst. mass: unstable.
4..	$P(C_2H_5)_4ICl_2$ .....	Alcohol on 3.....	—	Yellow crystals, stable.
5..	$P(C_2H_5)_4Br_7$ .....	Bromine on bromide	110°	Scarlet cryst. mass: unstable.
6..	$P(C_2H_5)_4Br_3$ .....	Alcohol on 5 or 9..	—	Red crystals: stable.
7..	$P(C_2H_5)_4Cl_3$ .....	Chlorine on chloride	110°	Yellow cryst. mass: unstable.
8..	$[P(C_2H_5)_4]_2SO_4Br_{22}$ (?) .	Bromine on sulphate	cold	Red liquid: unstable.
9..	$[P(C_2H_5)_4]_2SO_4Br_{12}$ ...	Bromine on sulphate	110°	Red solid: unstable.
10..	$[P(C_2H_5)_4]_2SO_4Cl_4$ ....	Chlorine on sulphate	130	Yellow solid: unstable.

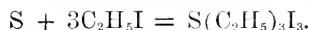
# XIX.—*Preparation of the Salts of Triethylsulphine, Tetrethylphosphonium, and Analogous Bases.*

By ORME MASSON, M.A., D.Sc. (Edin.), and J. B. KIRKLAND,  
University of Melbourne.

THE preparation of such a salt as triethylsulphine iodide in any quantity by the ordinary method, though easy in theory, is practically a most disagreeable operation, since it necessarily involves the making and manipulating a large amount of ethyl sulphide, or some equally objectionable substance. The preparation of analogous selenine salts by the ordinary method is open to a similar objection, which is, moreover, of greater weight on account of the still more noxious character of volatile selenium compounds; and there is, also, an additional disadvantage, in that a loss of the somewhat costly selenium in the preliminary operations is unavoidable. It is obvious that any method by which sulphur (or selenium) may be converted directly into sulphine (or selenine) salts, affording a good yield and avoiding the manipulation of noxious volatile substances, should be of value to chemists engaged in the study of such compounds.

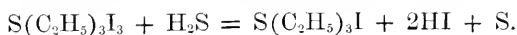
Klinger, 12 years ago, mentioned the fact (*Ber.*, **10**, 1880) that trimethylsulphine iodide could be obtained by heating sulphur in sealed tubes with methyl iodide and extracting the product with water. He did not, however, enter into details of the process, which has, so far as we are aware, not been made use of since then; nor was the method adopted by him sufficiently practical to replace that of von Oefele. We have found that the following method gives good results. It may be divided into three stages:—

(1.) Powdered roll sulphur is heated with ethyl iodide in sealed tubes at 180° for about 24 hours, the two substances being taken in the proportion of S : 3C<sub>2</sub>H<sub>5</sub>I, with a slight excess of the latter. Soft glass tubing may be employed, as there is only a little pressure when the tubes are opened (due to the formation of a combustible gas by a secondary reaction): we have adopted no special precautions to avoid the bursting of the tubes, and have not lost any. The sulphur entirely disappears, and the tubes, when cold, are seen to contain a large amount of a black tarry liquid, at once recognisable as a polyiodide by any one acquainted with such compounds. The reaction, in fact, may be correctly represented by the equation—



(2.) Klinger's method of extracting this substance with water could certainly not be worked satisfactorily, for such polyiodides are only

decomposed with difficulty by water, even on prolonged boiling. It is best to proceed as follows:—The contents of the tubes are washed into a tall glass cylinder, covered with water to a depth of some inches, and a current of hydrogen sulphide is then passed in through a tube which dips under the liquid polyiodide: by this means the latter is decomposed in the course of an hour or two. The action resembles that which occurs when hydrogen sulphide is led under the surface of bromine covered with water, except that no sulphuric acid is formed, as always happens in the latter case. When the polyiodide has disappeared, the vessel contains a clear acid solution of triethylsulphine iodide and hydrogen iodide, and a flocculent deposit of sulphur. The reaction is represented by the equation—



(3.) The solution decanted from the sulphur precipitate cannot be advantageously evaporated for the recovery of the sulphine salt, as this is attacked by the hydrogen iodide present. It is, therefore, mixed with excess of moist silver hydroxide, by which means a pure solution of triethylsulphine hydroxide is obtained; and this may then be converted into any desired salt by exactly neutralising it with the appropriate acid.

In our first experiment we thought to simplify matters and save silver by adding the silver hydroxide gradually to the acid solution until its reaction was neutral, so as to obtain the sulphine iodide at once by filtering and evaporating. It was found, however, that only a small quantity of the salt could be recovered in this way. As the silver iodide precipitate had been washed with boiling water until the washings were practically free from soluble iodide, the missing salt had to be looked for in the insoluble residue on the filter. Experiment showed that this, when treated with more moist silver hydroxide, yielded a quantity of the soluble alkaline sulphine hydroxide; so that it is evident that silver iodide and the sulphine iodide unite to form an insoluble double salt. This was further proved by mixing fresh moist silver iodide with a little solution of the sulphine iodide; the solution after a short time was found to give the iodine reaction only faintly. The silver iodide simultaneously changed in colour from yellow to white. The fact that the precipitate first formed when silver nitrate is added to a solution of an iodide is white, and become yellow only as the reagent is added in excess, is probably attributable to the same cause.

If the sulphine hydroxide solution is converted into the iodide by neutralisation with hydriodic acid, and this solution is evaporated to dryness, a yield is obtained which falls only a very little short of that calculated from the weight of sulphur employed, according to the

equations we have given. In one such experiment we obtained more than five-sixths of the theoretical yield. The following are the details of the experiment.

3·2 grams of powdered roll sulphur and 48 grams of ethyl iodide were heated in a sealed tube for 22 hours at 180—185°. Some combustible gas escaped when the tube was opened. The tarry polyiodide was washed out with water, and treated with a current of hydrogen sulphide for four hours in the manner described above. The solution was decanted from the precipitated sulphur; the latter was washed, and the washings added to the solution, which was then made up to a definite volume. The sulphur, after drying, weighed 3·5 grams. One-fourth of the solution was then treated with excess of moist silver hydroxide (from a weighed quantity of silver nitrate) in the cold, until a drop of it gave no iodine reaction; the mixture was then filtered, the silver iodide washed thoroughly with hot water, the washings being added to the filtrate. The filtrate and washings were then made up to a definite volume, and a small portion of it was titrated with standard hydrochloric acid. By this means it was found that, supposing the whole solution to have been treated with silver hydroxide, the sulphine hydroxide produced would have required 94 c.c. of normal hydrochloric acid for neutralisation, or would have weighed 12·8 grams. This result was checked by neutralising the remainder of the solution with hydriodic acid, evaporating to dryness, and weighing the sulphine iodide obtained. The weight was found to be 5·56 grams, which was equivalent to 22·68 grams, if the whole of the original solution had been treated in like manner. Finally, the iodide was recrystallised from alcohol (the equivalent of a total yield of 20 grams of pure salt was obtained), and its identity was established by an iodine estimation, although its properties left no doubt as to its true nature:—

Calculated for $S(C_2H_5)_3I$ .....	51·62 per cent. of I.
Found .....	51·60 „

The details of the experiment may be tabulated side by side with the figures calculated from the equations given above.

	Experi- ment.	Theory.
	grams.	grams.
S taken (and used up) .....	3·2	3·2
$C_2H_5I$ taken .....	48·0	46·8
S precipitated by the $H_2S$ action .....	3·5	3·2
Normal HCl required by the whole of the $S(C_2H_5)_3\cdot OH$ after $Ag_2O$ action .....	94 c.c.	100 c.c.
$S(C_2H_5)_3\cdot OH$ calculated from above. ....	12·8	13·6
$S(C_2H_5)_3I$ obtained (crude) .....	22·7	24·6

We have also ascertained by experiment that triethylselenine salts may be prepared by this method if selenium is used in place of sulphur. We have not made quantitative experiments, however, and so cannot state the yield obtainable.

The preparation of tetrethylphosphonium salts and their homologues is notoriously a troublesome matter, in spite of the classical researches of Hofmann, Cahours, and others. That this is so was shown in 1880 by Letts (*Trans. Roy. Soc. Edin.*, **30**, 185), who discussed at length the various processes then known, and rejected them all as uncertain, troublesome, and expensive. The well-known method of Hofmann, which consists in heating phosphonium iodide with absolute alcohol in sealed tubes at  $180^{\circ}$ , and acting on the resulting mixture of iodides with potash, so as to precipitate the tetrethylphosphonium iodide, &c., is generally considered the best process; but this was rejected by Letts; because he found it impossible to avoid the loss, by explosion, of the great majority of his tubes. We have not found this to be the case when the precautions mentioned by Hofmann are carefully attended to; but still we agree with Letts that the process is, at best, a very troublesome one; and it may be added that the preliminary preparation and preservation of large quantities of phosphonium iodide,  $\text{PH}_4\text{I}$ , constitute an undesirable factor. The method which we have adopted avoids all these disadvantages by making use of phosphorus itself and ethyl iodide as the raw materials, which are converted directly into a tetrethylphosphonium-derivative without risk of loss by explosions.

The practical details of the method are similar to those already described for the preparation of sulphine salts. Either ordinary phosphorus or red phosphorus may be used. Ethyl iodide is taken in excess of the proportion indicated by the formula  $7\text{C}_2\text{H}_5\text{I} + 2\text{P}$ ; we have found no harm result from using as much as  $6\text{C}_2\text{H}_5\text{I} : \text{P}$ ; the mixture is heated in sealed tubes at  $180^{\circ}$  for about 24 hours. When cold, the tubes are seen to contain a black tarry liquid or a semi-solid black crystalline mass of polyiodide, but no phosphorus. Combustible gas escapes on opening the tubes, but there is never enough pressure developed to cause explosions. The greater part of the excess of ethyl iodide may be recovered by distillation on a water-bath. The contents of the tubes are then reduced with hydrogen sulphide under water; and the clear acid solution, decanted from the precipitated sulphur, is treated with moist silver hydroxide in excess, so as to give a solution of the tetrethylphosphonium hydroxide. An alternative method of procedure in this case, however, may be employed with advantage; after the reduction with hydrogen sulphide, the excess of that gas is got rid of by a current of carbon dioxide, and the solution (containing the tetrethylphosphonium iodide and

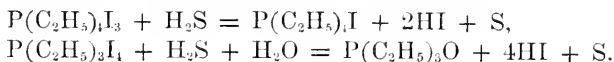
hydriodic acid) is saturated with potash and warmed. The result, as in Hofmann's method, is the separation of the phosphonium iodide, which floats as an oily layer on the potash; and it may be readily purified by crystallisation from alcohol. This method is indeed preferable to the other, as it does not involve the use of silver. It may also be stated that this potash method has been successfully applied to the preparation of triethylsulphine iodide; but it is doubtful whether in this case the yield obtained is as good as by the silver hydroxide process.

It is evident that the equation for the action of phosphorus on ethyl iodide cannot be so simple as that which we have shown to be true in the case of sulphur, for there is no polyiodide possible of the formula  $P(C_2H_5)_4I_4$ . It was thought that a mixture of the two polyiodides,  $P(C_2H_5)_4I_3$  and  $P(C_2H_5)_4I_5$ , might be produced, in which case the whole of the phosphorus would be eventually recoverable in the form of tetrethylphosphonium iodide. But experiments have proved that only half of this quantity can be actually obtained, while the other half of the phosphorus assumes a form which is converted during the treatment with hydrogen sulphide and water into triethylphosphine oxide. As this is a neutral substance, extremely soluble in water, and volatile in the steam produced by the evaporation of the solution, its formation is at first liable to be overlooked. Any theory of the reaction then, to be tenable, must, among other conditions, be such as to account for the conversion of one half of the phosphorus into a polyiodide of tetrethylphosphonium, and the other half into some substance of similar appearance, but convertible by water or hydrogen sulphide (or both acting together) into triethylphosphine oxide. These conditions are fulfilled by the following theory; and it will be further shown that most of the observed details of a quantitative experiment distinctly favour it, whilst they are not capable of equally satisfactory explanation in any other way.

(1.) The tarry product in the sealed tube consists of a mixture of the polyiodides of tetrethylphosphonium and triethylphosphine, produced according the equation—



(2.) When this mixture is treated with water and hydrogen sulphide, the following changes occur simultaneously:—



A solution is thus obtained containing hydrogen iodide, tetrethylphosphonium iodide, and triethylphosphine oxide; whilst sulphur is precipitated.

The following are the details of the experiment which suggested this theory:—

3.1 grams of phosphorus (in this case ordinary phosphorus was used; but it was afterwards found that red phosphorus would also answer) and 93.6 grams of ethyl iodide (equal to one-tenth of the weight in grams indicated by the formula  $P + 6C_2H_5I$ ) were heated for 22 hours at  $180-185^\circ$  in a sealed tube. All the phosphorus disappeared, and 30 grams of ethyl iodide was recovered by distillation of the contents of the tube. The black tarry product was completely decomposed in two hours by the hydrogen sulphide treatment, giving 3.4 grams of sulphur. One small portion of the solution (which was made up to a known volume) was titrated with standard alkali, and the total quantity of hydrogen iodide in solution was calculated from the result, and was found to be 33.6 grams. Another small portion was used for an estimation of the total iodine; and this, calculated for the whole quantity, was found to be 41.0 grams. The rest of the solution was treated with excess of moist silver hydroxide; and a portion of the filtrate and washings (made up to a known volume) was titrated with standard acid, and the total available hydroxide calculated from the result, and found to be 8.2 grams. The whole of the remainder of this alkaline solution was then neutralised with hydriodic acid, and evaporated on the water-bath; and the salt thus obtained was dried and weighed. From this, the total available iodide was calculated (allowance being made for those portions of the solution used for titration), and was found to amount to 13.45 grams. Finally this salt, which possessed all the properties of tetrethylphosphonium iodide, was crystallised from alcohol; and iodine estimations were made with crystals of two distinct crops for the purpose of complete identification:—

	Calculated for $P(C_2H_5)_4I$ .	Found.	
		I.	II.
Iodine, per cent. ....	46.35	45.98	45.90

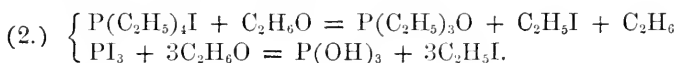
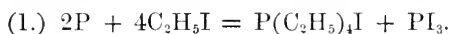
The triethylphosphine oxide was not saved or estimated in this experiment, as, indeed, its formation was not suspected until the results were calculated; but in a subsequent experiment the solution from the hydrogen sulphide action was distilled in such a manner as to permit of the oxide being collected and identified. The details of the above experiment are tabulated for the sake of comparison with the figures calculated from the theory which we have enunciated.



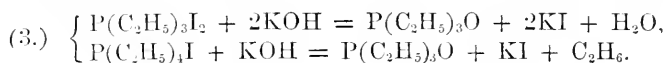
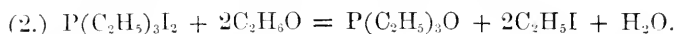
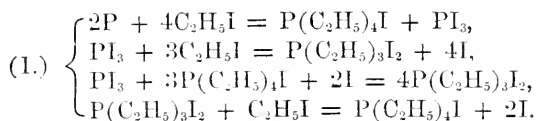
	Experiment.	Theory.
	grams.	grams.
P taken, and used up in the reaction .....	3.1	3.1
$\text{C}_2\text{H}_5\text{I}$ taken.....	93.6	—
$\text{C}_2\text{H}_5\text{I}$ recovered by distillation.....	30.0	—
$\text{C}_2\text{H}_5\text{I}$ used up (or lost) .....	63.6	51.6
S precipitated by the $\text{H}_2\text{S}$ action .....	3.4	3.2
Normal NaOH required for free HI .....	262.5 c.c.	300 c.c.
Total free HI deduced from above.....	33.6	38.4
Total iodine, as HI and $\text{P}(\text{C}_2\text{H}_5)_3\text{I}$ .....	41.0	44.4
Normal HCl required by the $\text{P}(\text{C}_2\text{H}_5)_3\text{OH}$ .....	50 c.c.	50 c.c.
Total $\text{P}(\text{C}_2\text{H}_5)_3\text{OH}$ formed, deduced from above .....	8.2	8.2
Total $\text{P}(\text{C}_2\text{H}_5)_3\text{I}$ produced (crude) .....	13.45	13.7
P not thus accounted for [ $\text{lost as P}(\text{C}_2\text{H}_5)_3\text{O}$ ] .....	1.58	1.55

This is not the first time that the action of phosphorus on ethyl iodide has been investigated, and a theory of the action advanced, although it is the first time, so far as we are aware, that it has been made use of for preparing the salts of tetrethylphosphonium. Carins (*Annalen*, **137**, 117) adopted the reaction as a means of preparing triethylphosphine oxide, and his method was further worked out by Crafts and Silva (this Journal, 1871, **24**, 629). Their procedure differed essentially from that described by us in the following particulars: The phosphorus and ethyl iodide were mixed in a very different proportion, viz.,  $2\text{P} : 5\text{C}_2\text{H}_5\text{I}$ . The phosphorus was not all consumed, some remaining in the amorphous form even after heating for 24 hours at  $175-180^\circ$ .

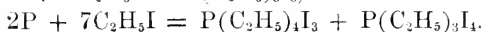
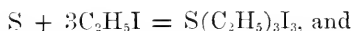
The iodine-coloured product was ground up with the residual phosphorus, and the whole distilled with alcohol till colourless. Ethyl iodide was produced in this reaction. The residue from the solution was found to contain phosphorous acid. The whole was then distilled in a copper retort with solid potash; when ethane, triethylphosphine, phosphine, and a large amount of triethylphosphine oxide were obtained. Carins proposed the following equations to represent (1) the action which occurs in the sealed tubes, (2) that which occurs when the product is treated with alcohol:—



Crafts and Silva rightly rejected these equations, but they retained the hypothesis of the formation of phosphorus triiodide. They proposed the following:—



As these equations have found their way into many text-books, and as we are convinced by our own experiments that they are erroneous, we venture to reproduce them here for the purpose of criticising them. The first four equations have never been supported by any experimental facts. The formation of phosphorus triiodide in particular is an assumption which the facts do not justify. The obvious polyiodide character of the product found in the reaction is entirely overlooked. The decolorisation by the subsequent distillation with alcohol was certainly due to the presence of the uncombined red phosphorus, as was the production of ethyl iodide and phosphorous acid; for polyiodides would act towards phosphorus and alcohol in the same manner as free iodine does; but no account is taken of this in the equations given. Had Crafts and Silva used a larger proportion of ethyl iodide, they would have got no residue of phosphorus; and the distillation with alcohol would have been ineffective. We feel convinced, moreover, that they would not have proposed the first set of equations, had they been sufficiently acquainted with the appearance of organic polyiodides to recognise the real nature of the contents of the tubes. Our experiments with both sulphur and phosphorus show that there is no reason for representing their reactions with ethyl iodide by more complicated equations than those we have given, viz. :—



XX.—CONTRIBUTIONS FROM THE LABORATORY OF  
GONVILLE AND CAIUS COLLEGE, CAMBRIDGE.

No. XIII. *On a Cubical Form of Bismuthous Oxide.*

By M. M. PATTISON MUIR, M.A., Fellow of Caius College, and ARTHUR HUTCHINSON, B.A., Scholar of Christ's College, Cambridge.

1. WHEN  $2\frac{1}{2}$  to 3 parts of potassium cyanide in concentrated aqueous solution are added to 1 part of bismuth nitrate dissolved in the smallest possible quantity of cold dilute nitric acid, a white precipitate of hydrated bismuthous oxide is obtained. About nine-tenths of the bismuth present as nitrate at the beginning of the reaction is precipitated as hydrated oxide; the addition of a very large excess of potassium cyanide fails to precipitate all the bismuth. If this precipitate is thoroughly washed, and then boiled with concentrated potassium cyanide solution, it remains unchanged.

2. When  $2\frac{1}{2}$  to 3 parts of potassium cyanide are added to a hot solution of 1 part of bismuth nitrate in the minimum quantity of nitric acid, a brownish-red precipitate is obtained; and in this case also about nine-tenths of the total bismuth is precipitated. The composition of this precipitate is represented by Baedeker to be  $\text{Bi}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$  (*Annalen*, **123**, 61); one of the present authors has described the precipitate as an oxycyanide of bismuth (*Proc. Roy. Soc. Edin.*, **11**, 557); and C. Hoffmann asserts that the substance is bismuth sulphide (*Annalen*, **223**, 110). When this puce-coloured precipitate is repeatedly treated with concentrated boiling potash solution, a deep-red liquid is produced, and a heavy, greyish-black solid remains.

3. Numerous specimens of this greyish-black solid have been prepared by us. In each case, from  $2$ — $2\frac{1}{2}$  parts of potassium cyanide were used for 1 part of bismuth nitrate; the liquids containing the precipitates were boiled for 10—15 minutes, and the precipitates allowed to settle; the supernatant liquids were poured off, and the precipitates were then heated with boiling potash (1 part of potash to 6 or 7 of water); as soon as the potash became coloured brownish-red it was poured off, and treatment with fresh quantities of boiling potash was continued till the liquid ceased to be coloured; the residues were then washed with boiling water until perfectly free from potash, that is, until the colour of slips of red litmus-paper was unaffected after the paper had remained in the liquid for about 12 hours; they were then dried at  $150$ — $170^\circ$ .

4. The substance thus prepared is a dark-grey, crystalline powder,

which is seen under the microscope to consist of small tetrahedra belonging to the cubic system; it is soluble with difficulty in acids; on heating in air, it turns yellow. Qualitative examination of the different specimens shewed—(1.) Absence of chlorine compounds. (2.) Absence of sulphur compounds. (3.) Presence of small traces of potassium, but absence of all other metals except bismuth. (4.) Presence of very small quantities of nitrogen and carbon. (5.) Presence of a little silica. And (6.) Presence of a little water.

Numerous quantitative analyses of the substance have been made.

*Bismuth* was estimated (1.) By heating the specimen in air, then dissolving in nitric acid, precipitating as carbonate, and weighing as  $\text{Bi}_2\text{O}_3$ . (2.) By fusing with potassium cyanide and weighing as Bi. (3.) By heating in air, dissolving in hydrochloric acid, precipitating as oxychloride, and weighing as  $\text{BiOCl}$ .

*Oxygen* was estimated by heating in pure hydrogen and weighing (1) the water formed, and (2) the residue left.

*Silica* was separated in the ordinary way during the course of the determination of bismuth by methods (1) and (3) above.

*Carbon* was estimated (1.) By heating in pure air, and leading the carbon dioxide (*a*) into a potash tube, weighed before and after the experiment; (*b*) into baryta-water, and determining the  $\text{BaCO}_3$  formed. (Dupré and Hake, *Jour. Chem. Soc. Trans.*, 1879, 159.) (2.) By heating in connection with a Sprengel pump, and measuring the carbon dioxide evolved. The percentage of carbon found ranged from 0.03 to 0.23.

Nitrogen was not estimated, as the qualitative examination showed it to be present in very minute quantities.

*Determination of Water*.—On heating in air, the substance turned yellow, and was converted into  $\text{Bi}_2\text{O}_3$ , this change being accompanied by slight loss of weight, which varied from 0.13 to 0.75 per cent., the mean being about 0.3 per cent.

When heated in a stream of dry nitrogen, quite free from oxygen and oxides of nitrogen, the substance does not turn yellow, but a loss of 0.5 per cent. (mean of several closely agreeing experiments) takes place; as this loss of weight was almost equal to the gain in the weight of a calcium chloride tube attached, the loss was shown to be due to the removal of a little water; at the same time, minute fragments of metallic bismuth were produced, due to the reducing action of traces of carbon present in the original substance.

We do not give details of our estimations as the experiments were so numerous; we rather present a condensed statement of the results.

I. The most trustworthy results for bismuth were obtained from a specimen prepared with great care, and which was specially well crystallised; several complete analyses of this were made, the sub-

stance being first heated in dry air, silica and potassium being determined in the residue.

$\text{Bi}_2\text{O}_3$  found varied from 97·45 to 98·10; mean = 97·81 per cent., which is equal to 87·67 per cent. Bi.

II.  $\text{SiO}_2$  varied from 1·1—1·2 Mean value = 1·13 per cent.

III. The amount of potassium found was equal to 6·45 per cent.  $\text{K}_2\text{O}$ .

IV. *Mean percentage of oxygen found by reducing in hydrogen, and deducting weight of residue from that of original.*

Two different specimens were used; the results varied from 10·58 to 11·34. Mean = 10·84 per cent.

V. *Mean percentage of oxygen found by reducing in hydrogen, and weighing water formed.*

Two different specimens were used; the results varied from 9·92 to 12·8. Mean = 10·87 per cent.

Some small part of the loss of weight observed when the substance was heated in hydrogen was doubtless due to removal of water associated with the silica and potassium compounds present, and a small part of the water obtained almost certainly came from this source; but the magnitude of the correction to be applied to the oxygen estimation on this account could not be accurately determined; it certainly did not exceed 0·3 per cent.

The results of the complete analysis of the greyish-black solid may then be stated as follows:—

Oxygen .....	10·85 (mean of many determinations made with different specimens).
Bismuth .....	87·51 (mean of 6 determinations made with the same specimen).
Silica .....	1·13 (mean of 6 determinations made with the same specimen).
Potash ( $\text{K}_2\text{O}$ ) .....	0·45 (mean of 3 determinations made with the same specimen).
Water (approx.) .....	0·30 (mean of many determinations made with different specimens).
C and N (approx.) ...	0·20 (N not determined; mean per cent. of C from different specimens = 0·125).
	<hr/> 100·44

If a correction is made on the bismuth for the quantities of silica, potash, water, carbon, and nitrogen, we have:—

		Calculated for $\text{Bi}_2\text{O}_3$ .	
Bismuth . . . . .	89.46	Bismuth . . . . .	89.65
Oxygen. . . . .	10.85	Oxygen . . . . .	10.35
<hr/>		<hr/>	
100.31		100.00	

5. When the greyish-black substance, which we have proved to consist almost entirely of bismuthous oxide, was heated to redness in air or in a stream of oxygen, it rapidly changed to the colour and appearance of ordinary bismuthous oxide. This colour change was accompanied by a loss of weight amounting to about 0.3 per cent. (see paragraph 4).

Microscopical examination showed that the greyish-black compound and the yellow substance remaining on heating in air were identical in crystalline form, and consisted of minute regular tetrahedra. The sharpness of the outlines and the brightness of the faces of the tetrahedrons remained unaffected by heating, the only change visible to the eye being that of colour.

The change produced on heating in air or oxygen almost certainly consists in the oxidation of a minute quantity of the puce-coloured compound formed by the reaction of potassium cyanide with bismuth nitrate. This small quantity of the compound in question adheres most persistently to the tetrahedral crystals of the bismuthous oxide. When the greyish-black crystals are heated in nitrogen, the colour does not change, but a very little bismuthous oxide is reduced to bismuth (see paragraph 4); in this case the adhering film of the compound containing carbon and nitrogen is not burnt away, but some of it reacts with the bismuthous oxide, which it reduces to metal.

We found that it is possible to remove the whole of the puce-coloured compound containing carbon and nitrogen by prolonged treatment with boiling potash solution so concentrated that it solidifies on cooling; the residual product is the pale yellow bismuthous oxide. Specimens thus prepared and dried at  $160^\circ$  did not undergo any change in weight when heated to full redness in air. The long-continued boiling with very concentrated potash tends to corrode the cubical crystals, and produce needles, apparently rhombic, which are contaminated with much silica.

6. We find that the best method of obtaining cubical bismuthous oxide is to prepare the grey substance as described in paragraph 3, and then to heat this in air till it turns yellow. The oxide thus prepared is pale buff-yellow; it consists of minute but well-developed regular tetrahedra, the faces of these are very smooth and bright, and their edges are in some cases modified by the cube planes, or in crystallographic notation the crystals exhibit the form  $k\{111\}$  and  $\{100\}$  of the cubic system.

According to Nordenskjöld (*Pogg. Ann.*, **114**, 512), bismuthous oxide crystallises in rhombic prisms; the ratio of the axes given by him is not identical with the ratio for either arsenious or antimonious oxide, but the three oxides are probably isomorphous in the usual acceptance of this term.

It is, moreover, well known that antimonious and arsenious oxides are also dimorphous, crystallising in the cubic as well as in the rhombic system (Malard is, however, of opinion that the apparently cubic crystals of antimonious oxide are in reality built up of individuals belonging to the oblique system). The cubic crystals of these two oxides are usually octahedra, but arsenious oxide sometimes crystallises in tetrahedra also, and we may therefore consider that the preparation by us of tetrahedral bismuthous oxide establishes in a broad sense the isodimorphism of this group of oxides, as is seen in the following table:—

Arsenious oxide	{ rhombic; prisms, 0.3758 : 1 : 0.35; sp. gr. 4.2; cubic; octahedra and tetrahedra; sp. gr. 3.689.
Antimonious oxide	{ rhombic; prisms, 0.394 : 1 : 1.414; sp. gr. 5.5; cubic; (?) octahedra; sp. gr. 5.1.
Bismuthous oxide	{ rhombic; prisms, 0.8165 : 1 : 1.064; sp. gr. 8.3; cubic; tetrahedra; sp. gr. 8.828.

Cubical bismuthous oxide is specifically heavier than the rhombic form. The sp. gr. of the specimen prepared by us was found to be 8.828 at 25°, referred to water at the same temperature (mean of several closely agreeing determinations made with different specimens). Herapath (*Phil. Mag.*, **64**, 321 [1824]) gave the value 8.21; Karsten (*Schweigger's Journ.*, **65**, 320, 394 [1832]) gave 8.173; Playfair and Joule (*Chem. Soc. Mem.*, **3**, 57 [1848]) gave 8.979; and Le Royer and Dumas gave 8.45 (see Playfair and Joule). The mean of these values is 8.304.

7. We have endeavoured to trace the reactions by which the cubical form of bismuthous oxide is produced, but we have not yet succeeded in fully elucidating the stages of the process. Our experiments have shown: (1.) That the tetrahedral crystals are formed in the largest quantity under the conditions described in paragraph 3. (2.) That if the precipitate is thoroughly washed before it is heated with potash very few tetrahedra are formed. (3.) That if this precipitate is not washed but is kept in contact with very concentrated potash solution for several weeks in the cold, a few tetrahedra are formed.

We have also found that the puce-coloured precipitate produced by potassium cyanide is amorphous.

Repeated experiments have convinced us that the action of hot potash on this amorphous precipitate frequently results in the formation not only of tetrahedra, but also of needles which are perhaps rhombic prisms, and also of more or fewer twin-crystals somewhat of this form—



In some cases the product consisted mainly of these twins, in some the twins were mixed with needles, and in some the product was mostly composed of tetrahedra.

Analyses detailed by one of us (*Proc. Roy. Soc. Edin.*, **11**, 557) led to the conclusion that the puce-coloured precipitate is an oxycyanide of bismuth. More recent analyses, and an examination of the action of acids on this precipitate, lead us to say rather that it is a compound of bismuth, oxygen, carbon, and nitrogen. When this precipitate is boiled with concentrated potash solution, 2–3 per cent. of the bismuth in the substance goes into solution along with practically all the carbon and nitrogen. Neutralisation of the deep red liquid thus obtained produces a red-brown solid which contains bismuth, carbon, nitrogen, and water. Analyses of this solid have led to conflicting results; it does not give the reactions of a cyanide, and the nitrogen and carbon are present in approximately the ratio 1 : 1·4, whereas in cyanogen they are present in the ratio 1 : 0·857.

We reserve an account of the puce-coloured precipitate and of the red-brown solid until we have examined them more fully.

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## XXI.—CONTRIBUTIONS FROM THE LABORATORY OF GONVILLE AND CAIUS COLLEGE, CAMBRIDGE.

### No. XIV. *Periodates*. Part II.

By C. W. KIMMINS, M.A., D.Sc., late Scholar of Downing College,  
Cambridge.

In a previous paper on this subject (*this Journal*, Trans., 1887, 356) I described the preparation and examination of certain periodates of sodium, potassium, and silver, and expressed my intention of in-



vestigating the periodates of other metals with a view to obtain evidence as to the constitution of these compounds.

I have now prepared periodates of lead, iron, copper, nickel, and cadmium, by reactions between soluble salts of these elements and solutions of periodates of sodium and potassium, and I have made direct determinations of the metal and iodine in each salt. (For methods of analysis, see Appendix.)

### *Periodates of Lead.*

*a.*  $\text{Pb}_3\text{H}_4(\text{IO}_6)_2$ .—On treating a solution of  $\text{Na}_2\text{H}_3\text{IO}_6$  with lead nitrate, a light yellow, amorphous salt is obtained,  $\text{Pb}_3\text{H}_4(\text{IO}_6)_2$ . The same salt is obtained by using  $\text{K}_4\text{I}_2\text{O}_9$  instead of the sodium salt.

	Calculated. $\text{Pb}_3\text{H}_4(\text{IO}_6)_2$ .	Found.	
		I.	II.
Pb . . . . .	57.86 p. c.	57.86	57.51 p. c.
I . . . . .	23.78 „	24.01	— „

*b.*  $\text{Pb}_3(\text{IO}_5)_2$ .—On dissolving  $\text{Pb}_3\text{H}_4(\text{IO}_6)_2$  in nitric acid, and concentrating the solution, it is converted into a dark yellow powder, having the composition  $\text{Pb}_3(\text{IO}_5)_2$ .

	Calculated. $\text{Pb}_3(\text{IO}_5)_2$ .	Found.	
		I.	II.
Pb . . . . .	59.89 p. c.	59.85	59.99 p. c.
I . . . . .	24.61 „	23.1	— „

On treating sodium and potassium periodates with nitric acid of different degrees of concentration, and then adding lead nitrate, the periodate,  $\text{Pb}_3(\text{IO}_5)_2$ , was in all cases obtained.

*c.*  $\text{Pb}(\text{IO}_4)_2$ .—If  $\text{Pb}_3\text{H}_4(\text{IO}_6)_2$  or  $\text{Pb}_3(\text{IO}_5)_2$  is boiled for some time with concentrated nitric acid, a small quantity of an amorphous red salt is obtained, which can be separated from the yellow salt only with difficulty. Analysis of this salt points clearly to the composition  $\text{Pb}(\text{IO}_4)_2$ , but it could not be obtained quite pure.

The salt,  $\text{Pb}_3(\text{IO}_5)_2$ , readily takes up moisture;  $\text{Pb}_3\text{H}_4(\text{IO}_6)_2$  does not.

On keeping  $\text{Pb}_3\text{H}_4(\text{IO}_6)_2$  at  $275^\circ$  for four hours it gave off water, and was converted into  $\text{Pb}_3(\text{IO}_5)_2$ .



### *Periodates of Iron.*

*Ferric Salts.*—*a.*  $\text{FeHI}_2\text{O}_9$ .—On treating a solution of  $\text{Na}_2\text{H}_3\text{IO}_6$  with ferric chloride, a light brown precipitate is formed, which at

100° gives off water, and forms a reddish-brown powder of the composition  $\text{FeHI}_2\text{O}_9$ . The same salt is formed when  $\text{K}_4\text{I}_2\text{O}_9$  is used in place of  $\text{Na}_2\text{H}_3\text{IO}_6$ .

	Calculated. $\text{FeHI}_2\text{O}_9$ .	Found.
Fe.....	21.96 per cent.	22.23 per cent.
I .....	49.92     ,,	49.48     ,,

Boiling with dilute nitric acid appears to have no effect on this salt. The results of several analyses gave the same composition as above.

*b.*  $\text{Fe}(\text{IO}_4)_3$ .—On boiling  $\text{FeHI}_2\text{O}_9$  for some time with concentrated nitric acid, a bright yellow powder is formed, which has the composition  $\text{Fe}(\text{IO}_4)_3$ .

*Ferrous Salts.* *a.*  $\text{Fe}_3(\text{IO}_6)_2$ .—On treating a solution of  $\text{K}_4\text{I}_2\text{O}_9$  with ferrous sulphate, a brick-red, crystalline salt is produced, having the composition  $\text{Fe}_3(\text{IO}_6)_2$ .

	Calculated. $\text{Fe}_3(\text{IO}_6)_2$ .	Found.
Fe.....	38.58 per cent.	38.05 per cent.

*b.*  $\text{FeH}_3\text{IO}_6$ .—This salt is produced by adding a solution of  $\text{Na}_2\text{H}_3\text{IO}_6$  to ferrous sulphate. It is a light brown powder.

	Calculated. $\text{FeH}_3\text{IO}_6$ .	Found.
Fe.....	19.93 per cent.	20.18 per cent.

The determination of iodine in the ferrous salts, in both cases, was rather less than the calculated values.

#### *Periodates of Copper.*

$\text{Cu}_2\text{HIO}_6$ .—On acting upon  $\text{Na}_2\text{H}_3\text{IO}_6$  solution with copper sulphate, and boiling, a bright green, crystalline salt separates out, which has the composition  $\text{Cu}_2\text{HIO}_6$ . A solution of  $\text{K}_4\text{I}_2\text{O}_9$ , similarly treated, gives the same salt, and also a more soluble one, which appears on concentrating the solution (I was not able to get sufficient of this latter salt to obtain a satisfactory analysis).

	Calculated. $\text{Cu}_2\text{HIO}_6$ .	Found.
Cu .....	35.99 per cent.	35.63 per cent.
I .....	36.1     ,,	38.81     ,,

This salt is very soluble in nitric acid, and on concentrating this solution a bright yellow, crystalline salt is formed, but it could not be obtained sufficiently pure for analysis.

*Periodates of Nickel.*

*a.*  $\text{Ni}_3(\text{IO}_5)_2$ .—This compound is obtained as a greenish-yellow, amorphous salt by the action of nickel sulphate on a solution of  $\text{Na}_2\text{H}_3\text{IO}_6$ . No action takes place in the cold, but, on boiling, the salt separates out as a flocculent precipitate.

Calculated.		Found.	
$\text{Ni}_3(\text{IO}_5)_2$ .		I.	II.
Ni .....	29.8 p. c.	29.54	29.36 p. c.

*b.*  $\text{Ni}_2\text{I}_2\text{O}_9$ .—On treating a solution of  $\text{K}_4\text{I}_2\text{O}_9$  with nickel sulphate, a bluish-green gelatinous precipitate is formed, which, on drying at  $100^\circ$ , gives a black crystalline salt having the composition  $\text{Ni}_2\text{I}_2\text{O}_9$ .

Calculated.		Found.
$\text{Ni}_2\text{I}_2\text{O}_9$ .		
Ni .....	22.75 per cent.	22.32 per cent.

The determinations of iodine, in each case, were rather below the calculated values.

No other salt could be obtained on boiling down the nickel periodates with concentrated nitric acid.

*Periodates of Cadmium.*

$\text{CdHIO}_5$ .—This salt is readily obtained from  $\text{Na}_2\text{H}_3\text{IO}_6$  solution on treatment with cadmium sulphate, and with some difficulty from  $\text{K}_4\text{I}_2\text{O}_9$ . It is a light brown powder.

Calculated.		Found.
$\text{CdHIO}_5$ .		
Cd .....	34.9 per cent.	34.43 per cent.
I .....	39.69 „	39.78 „

No other salt of this metal could be obtained.

*Periodates of Potassium.*

It was stated in a previous paper (this Journal, Trans., 1887, 365), that on passing chlorine through a solution of equal weights of potassium iodate and caustic potash,  $\text{KIO}_4$  was obtained, and that  $\text{K}_4\text{I}_2\text{O}_9$  separated out from the solution on concentration. I now find that  $\text{K}_4\text{I}_2\text{O}_9$  is soluble in caustic potash solution, whilst  $\text{KIO}_4$  is almost insoluble, and that if a smaller quantity of caustic potash is used, or if the excess of caustic potash, after separation of  $\text{KIO}_4$ , is exactly

neutralised with nitric acid, the salt  $K_4I_2O_9 \cdot 3H_2O$ , mentioned by Ram-melsberg, is readily obtained *without concentration*. If excess of acid is used, the salt  $K_3HI_2O_9$  is obtained.

### *Periodates of Silver.*

The salts of this metal, mentioned in my former paper, were all obtained from the sodium salt,  $Na_2H_3IO_6$ . I have since made experiments, using  $K_4I_2O_9$  instead of the sodium salt, and I find that a similar series of salts may be obtained, and in the same order, by using nitric acid of different degrees of concentration. The salts obtained are  $Ag_2HIO_5$ ,  $Ag_2H_3IO_6$ ,  $Ag_3H_2IO_6$ , and  $AgIO_4 \cdot H_2O$ ; but in addition to these,  $Ag_4I_2O_9 \cdot 3H_2O$  is readily obtained by the direct action of nitrate of silver on solution of  $K_4I_2O_9$  in presence of nitric acid.

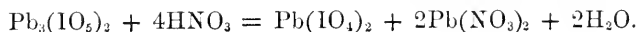
The first salt obtained by the action of silver nitrate on soluble periodates is generally stated to be  $Ag_3IO_6$ ; but with  $K_4I_2O_9$ , as with  $Na_2H_3IO_6$ , I failed to prepare this salt; in each case I obtained  $Ag_2HIO_5$ .

The following is a list of the salts I have prepared and analysed:—

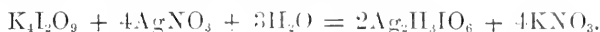
Meta-periodates ( $HIO_4$ ).	Meso-periodates ( $H_3IO_5$ ).	Para-periodates ( $H_5IO_6$ ).	Di-periodates. ( $H_7I_2O_9$ ).
$KIO_4$ $AgIO_4 \cdot H_2O$ $AgIO_4$ $Pb(IO_4)_2$ $Fe(IO_4)_3$	$Ag_2HIO_5$ $Pb_3(IO_5)_2$ $Ni_3(IO_5)_2$ $CdHIO_5$	$Na_2H_3IO_6$ $Na_3H_3IO_6$ $Ba_5(IO_6)_2$ $Ag_2H_3IO_6$ $Ag_3H_2IO_6$ $Pb_3H_4(IO_6)_2$ $Fe_5(IO_6)_2$ $FeH_3IO_6$ $Cu_2HIO_6$	$K_4I_2O_9$ $K_3HI_2O_9$ $Ag_4I_2O_9 \cdot 3H_2O$ $Ag_4I_2O_9 \cdot H_2O$ $Ag_4I_2O_9$ $FeHI_2O_9$ $Ni_2I_2O_9$

*The Constitution of the Periodates.*—It is evident that it is quite easy to pass from one series of periodates to the other, and that the result of boiling down with nitric acid is to convert di-, meso-, and para-periodates into meta-periodates. This is well shown in the case of the silver salts, silver nitrate being generally formed, as in the case of  $Ag_2H_3IO_6$ ;  $Ag_2H_3IO_6 + HNO_3 = AgIO_4 \cdot H_2O + H_2O + AgNO_3$ .

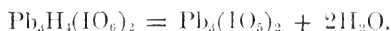
Similarly, in the case of the lead salts, a quantity of lead nitrate separates out after the formation of lead meta-periodate,



The conversion of di-periodates into para-periodates is shown by the action of silver nitrate on  $K_4I_2O_9$ ;



The conversion of para-periodates into meso-periodates may be brought about by heating acid para-periodates; for example



On heating  $Ag_2HIO_5$  to a high temperature,  $300^\circ$ , it loses weight and water is given off; the change which takes place is probably represented by the following equation:—



Thus a meso-periodate is converted directly into a di-periodate.

By heating acid periodates, changes may be brought about similar to those which take place on heating certain acid phosphates and in which ortho-phosphates are converted into pyro- or meta-phosphates.

Thomsen, from thermal considerations, regards the periodates as being all of one type,  $R_4I_2O_9 \cdot 3H_2O$ ; these he would call normal periodates, and those in which more hydrogen is replaced he distinguishes as mono-, di-, and tri-basic, for example,  $Ba_5(IO_6)_2$ , would be written  $Ba_3I_2O_9 \cdot 3BaO$ . There appears to be a great difference, however, between the water of crystallisation and that which is given off on heating the acid salts. The water in the former case appears to be in a much less stable combination. Thus at  $100^\circ$  the water of crystallisation in most cases is driven off, and in no case does it require a higher temperature than  $130^\circ$ . Rammelsberg states (*Pogg. Ann.*, **134**, 368) that  $Ag_4I_2O_9 \cdot H_2O$  requires a higher temperature,  $150^\circ$ , but I find that if kept at  $130^\circ$  for 12 hours the whole of the water is removed. In the case of acid salts, however, no water is given off until a temperature of  $270$ — $300^\circ$  is reached, and in some cases a still higher temperature is required.

If Thomsen's views are accepted one would expect the salts  $Ag_3HIO_5$  and  $Ag_4I_2O_9 \cdot H_2O$ , prepared by different methods, to be the same; but they differ in appearance and behaviour. On heating  $Ag_4I_2O_9 \cdot H_2O$ , the whole of the water is removed; in the case of the meso-salt, no change takes place below  $300^\circ$ .

Similarly,  $Ag_2H_3IO_6$  and  $Ag_4I_2O_9 \cdot 3H_2O$  are quite distinct in their chemical and physical properties.

On treating solutions of  $Na_2H_3IO_6$  and  $K_4I_2O_9$  with soluble salts of certain metals, insoluble periodates are obtained which differ in many cases according to the alkali periodate used. If, however, the alkali

periodates  $\text{Na}_2\text{H}_3\text{IO}_6$  and  $\text{K}_4\text{I}_2\text{O}_9 \cdot 3\text{H}_2\text{O}$  are of the same type, the same salt would probably result.

The ready way in which salts of one series pass into those of another series, as shown, for example, by the preparation of the silver periodates, may account for the remarkable thermal results observed by Thomsen on adding potassium hydrate to para-periodic acid; thus—

First formula-weight of potash produced	5150	gram-units of heat.
Second                   "                   "                   "	21440	"                   "
Third                   "                   "                   "	3150	"                   "
Fourth and fifth formula-weights of potash added .....	2300	"                   "

The general tendency of the action of nitric acid is first to remove water and then to convert the resulting periodates into the meta-salts, often with separation of part of the metal as nitrate, as in the cases of silver and lead.

There can be little doubt, therefore, that there are four distinct series of salts; and I propose to attempt the preparation of meta- and meso-periodic acids from the corresponding salts.

I must again express my thanks to Mr. Pattison Muir for continual help and suggestions.

### *Appendix.*

*Method of Analysis.*—The method of estimating iodine was as described in my previous paper. It is necessary to make a blank experiment with measured quantities of potassium iodide solution and hydrochloric acid, and to allow for any iodine set free on digesting for six hours.

In one case, when an unusually large quantity of iodine was set free, the quantity was found to be only six equivalents of the iodine in the substance; this was probably due to iodide of chlorine not being split up by the potassium iodide. Unless periodates of metals of high atomic weight are being analysed, not more than 0.3 gram should be used with a bottle of 250 c.c. capacity. The lead was estimated as sulphate, by treating with sulphuric acid and embedding the crucible deep in a sand-bath. By this method, analyses rarely differed more than 0.15 per cent. A similar method was used for the estimation of silver as chloride.

XXII.—CONTRIBUTIONS FROM THE LABORATORY OF  
GONVILLE AND CAIUS COLLEGE, CAMBRIDGE.XV. *A Compound of Boric Acid with Sulphur Trioxide.*

By R. F. D'ARCY, B.A.

BORON oxide is one of the few oxides which is stated to behave sometimes as an acidie and sometimes as a basic oxide. The evidence in favour of the latter statement is obtained from the isolation of the following compounds:—(1) a very stable compound, whose composition is represented by the formula  $\text{BPO}_4$  (Gustavson, *Ber.*, **3**, 426 **4**, 976); and (2) a compound analogous to tartar emetic, but containing boron instead of antimony (Sonbeiran and Capitaine, *J. Pharm.*, **25**, 741; Duflos, *Schweigger's J.*, **64**, 333, &c.).

In addition to these compounds of boric acid with sulphur trioxide and sulphuric acid have been described. Merz (*J. pr. Chem.*, **99**, 181) stated that a substance having the composition corresponding to the formula  $5\text{B}_2\text{O}_3, 2\text{SO}_3, 2\text{H}_2\text{O}$  [ $\text{SO}_3$  29·31;  $\text{B}_2\text{O}_3$  64·10;  $\text{H}_2\text{O}$  6·59] could be obtained by heating boric acid with excess of sulphuric acid at 250—280°. Merz obtained this compound several times, but in certain cases nearly all the sulphuric acid was evolved.

Schultz-Sellaek (*Ber.*, **4**, 15) states that crystals separate from a solution of  $\text{B}_2\text{O}_3$  in fuming sulphuric acid, and that the composition is represented by the formula  $\text{B}_2\text{O}_3, \text{H}_2\text{O}, 3\text{SO}_3$ . He analysed this substance by estimating the amount of sulphuric acid as  $\text{BaSO}_4$ , the water directly, and the  $\text{B}_2\text{O}_3$  by difference. The percentage composition according to this formula is—

$\text{SO}_3$ .....	73·2
$\text{B}_2\text{O}_3$ .....	21·3
$\text{H}_2\text{O}$ .....	5·5

Experimenting as Merz did, I, like Schultz-Sellaek, failed to get the substance Merz described; as the temperature rose, sulphur trioxide was evolved continuously, and no compound of definite composition could be obtained in this manner.

I next tried to obtain the substance described by Schultz-Sellaek, but failed to obtain a crystalline compound. I then added finely powdered boric acid to a large quantity of  $\text{SO}_3$ ; a rather violent reaction ensued, the whole liquefied, and was mixed by stirring; the mixture was then heated at 100° until sulphur trioxide ceased to be evolved. On cooling, a solid separated, and this was dried on tiles in desiccators over sulphuric acid.

I have analysed substances prepared in this manner, by determining the sulphur trioxide as  $\text{BaSO}_4$  by precipitation with  $\text{BaCl}_2$ , the boron trioxide by the methyl alcohol method (Gooch, *Proc. Amer. Acad. of Arts and Sciences*, 1886-1887), and the water by difference. It was an advantage to be able to determine the boron trioxide directly; the estimations by the methyl alcohol method seemed to be satisfactory; different analyses of the same substance gave results which never differed by as much as 0.5 per cent.

The following are the details of the substances so prepared:—

1. 2 grams of boric acid were added to 13.2 grams of sulphur trioxide. The substance obtained from these as described above gave on analysis the following numbers:—

$\text{SO}_3$ . . . . .	78.8
$\text{B}_2\text{O}_3$ . . . . .	11.3
$\text{H}_2\text{O}$ . . . . .	9.9

2. From 2.2 grams of boric acid and 23.2 grams of sulphur trioxide, a substance was obtained possessing the composition—

$\text{SO}_3$ . . . . .	79.7
$\text{B}_2\text{O}_3$ . . . . .	10.6
$\text{H}_2\text{O}$ . . . . .	9.7

3. From 7 grams of boric acid and 35 grams of sulphur trioxide a substance was obtained which possessed the following percentage composition:—

$\text{SO}_3$ . . . . .	78.3
$\text{B}_2\text{O}_3$ . . . . .	12.2
$\text{H}_2\text{O}$ . . . . .	9.5

None of these differs much from—

$\text{SO}_3$ . . . . .	79.5
$\text{B}_2\text{O}_3$ . . . . .	11.6
$\text{H}_2\text{O}$ . . . . .	8.9

which is the percentage composition corresponding to the formula  $\text{BH}_3\text{O}_3, 3\text{SO}_3$  or  $\text{B}(\text{HSO}_4)_3$ .

The substance thus prepared is a white solid, which melts at about  $215^\circ$ , and dissolves readily in fuming sulphuric acid. It is very hygroscopic, and this possibly explains why the analyses do not agree better.

It is worthy of notice that, in preparing the above substance, the proportions of boric acid and sulphur trioxide used varied from about 1 : 5 to 1 : 12. In order to vary the conditions further, the following experiment was made:—5 c.c. of concentrated sulphuric acid and



6 grams of boric acid were added to 115 grams of sulphur trioxide, and the mixture was heated till sulphur trioxide ceased to be evolved. A solid separated out on standing; on analysis, this solid was found to have the following percentage composition:—

$\text{SO}_3$ .....	80.1
$\text{B}_2\text{O}_3$ .....	11.8
$\text{H}_2\text{O}$ .....	8.1

which agrees very fairly with the composition given by the formula stated above.

So far as my experiments have gone,  $\text{SO}_3$  and dry  $\text{B}_2\text{O}_3$  do not seem to combine when heated together.

The compound  $\text{B}(\text{HSO}_4)_3$  may be a salt of  $\text{H}_2\text{SO}_4$ , or it may be a compound of  $\text{H}_3\text{BO}_3$  with  $\text{SO}_3$ , somewhat analogous to the compounds of  $\text{WO}_3$  and  $\text{MoO}_3$  with anhydrides. If the presence of water is necessary for the formation of the compound, the latter view seems to be preferable to the former.

I hope to continue this work, and, if possible, to obtain similar compounds with other acids and acidic oxides, and to investigate their properties.

I have much pleasure in thanking Mr. Pattison Muir, at whose suggestion I undertook this work, for help during the course of these experiments.

### XXIII.—CONTRIBUTIONS FROM THE LABORATORY OF GONVILLE AND CAIUS COLLEGE, CAMBRIDGE.

#### No. XVII.—*On Compounds of Arsenious Oxide with Sulphuric Anhydride.*

By R. H. ADIE, B.A., Scholar of Trinity College.

1. THE conditions which determine the formation and stabilities of the class of bodies known as “molecular compounds,” have not yet been fully elucidated. It seemed probable that a comparison of the corresponding compounds of a group of allied elements would throw some light on this subject. With this aim in view, I have selected the fifth group, as the elements are classified on the basis of the periodic law, and I propose, in the first instance, to examine some of the analogous compounds which the oxides of these elements form with anhydrides.

To make a beginning, I have studied the bodies formed by the combination of arsenious oxide with sulphur trioxide.

2. In 1863, Richter found masses of arsenious oxide, containing sulphuric acid, deposited in the flues leading from the pyrites burners to the chamber of a sulphuric acid manufactory. These crystals were analysed by Reich (*J. pr. Chem.*, **90**, 176), who found in them 72.18 per cent. of  $\text{As}_2\text{O}_3$ . He states that they were completely decomposed by heating. Schafhäütl (*Berzel. Jahr.*, **22**, 113) also obtained a compound of arsenious oxide with sulphuric anhydride, from the flues of a sulphuric acid works. By dissolving arsenious oxide in fuming sulphuric acid of a strength not specified, Schultz-Sellack, in 1871, obtained crystals the analysis of which agreed with the formula  $\text{As}_2\text{O}_3 \cdot 4\text{SO}_2$  (*Ber.*, **4**, 169); these crystals were readily decomposed by water. In 1886 (*Ber.*, **19**, 3185), R. Weber obtained two compounds,  $\text{As}_2\text{O}_3 \cdot 3\text{SO}_3$  and  $\text{As}_2\text{O}_3 \cdot 6\text{SO}_3$ , by heating together the two oxides and distilling off the excess of sulphuric anhydride at definite temperatures.

3. As the products of the reaction of arsenious oxide with sulphuric acid of varying degrees of concentration do not appear to have been examined, I began by using concentrated sulphuric acid (about 98 per cent.  $\text{H}_2\text{SO}_4$ ), and then I examined the effects of diluting this acid; I also used fuming sulphuric acid and liquid  $\text{SO}_3$ .

4. In each case the acid was heated to boiling, and powdered arsenious oxide was dropped in so long as it continued to be dissolved; the crystals which formed on cooling were drained, at once pressed repeatedly between porous tiles which had been thoroughly dried, and analysed. In some cases, second crops of crystals were obtained by agitating the mother-liquors, or by allowing them to remain over fuming sulphuric acid. In one or two cases, the crystals were recrystallised from acid of the same concentration as that from which they had separated. In this section, I give a general account of the concentrations of the acids employed and the compositions of the compounds obtained; the analytical details are presented in section 6.

A. Sulphuric anhydride used; solution effected by heating in a closed tube at  $100^\circ$ . Compound obtained  $\text{As}_2\text{O}_3 \cdot 8\text{SO}_3$ , perhaps mixed with  $\text{As}_2\text{O}_3 \cdot 9\text{SO}_3$ .

B. Nordhansen acid used, containing 88.3 per cent.  $\text{SO}_3$ , and therefore approximating to the composition  $2\text{H}_2\text{SO}_4 \cdot \text{SO}_3$ ; crystals recrystallised from the same acid.

Compound obtained  $\text{As}_2\text{O}_3 \cdot 4\text{SO}_3$ ; previously obtained by Schultz-Sellack (section 2). The mother-liquor placed in an exsiccator on one occasion deposited crystals which approxi-

mated in composition to  $\text{As}_2\text{O}_3 \cdot 3\text{SO}_3$ ; these crystals were recrystallised from "concentrated sulphuric acid"; the composition of the compound which separated was  $\text{As}_2\text{O}_3 \cdot 2\text{SO}_3$ , which is the same as that of the compound formed when arsenious oxide is dissolved in hot concentrated sulphuric acid (see C). The mother-liquor from the  $\text{As}_2\text{O}_3 \cdot 2\text{SO}_3$  deposited crystals containing rather more  $\text{SO}_3$  than is required by the formula  $\text{As}_2\text{O}_3 \cdot 2\text{SO}_3$ .

- C. Concentrated sulphuric acid used, containing about 98 per cent.  $\text{H}_2\text{SO}_4$ ; two crops of crystals were obtained. The first crop contained less  $\text{SO}_3$  than is required by the formula  $\text{As}_2\text{O}_3 \cdot 2\text{SO}_3$ , and more than corresponds to the formula  $\text{As}_2\text{O}_3 \cdot \text{SO}_3$ ; probably the excess of arsenious oxide dissolved at the higher temperature crystallised out along with varying quantities of  $\text{SO}_3$ . The second crop of crystals agreed with the formula  $\text{As}_2\text{O}_3 \cdot 2\text{SO}_3$ ; recrystallisation scarcely affected the composition of these crystals.
- D. Sulphuric acid of different concentrations was used; the concentrations are approximately expressed by the formulae  $9\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ ,  $9\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ ,  $9\text{H}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , and  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ . In each case, the compound  $\text{As}_2\text{O}_3 \cdot \text{SO}_3$  was produced; previously obtained by Richter and analysed by Reich (see section 2). No compound of  $\text{As}_2\text{O}_3$  with  $\text{SO}_3$  was obtained by dissolving arsenious oxide in acid more dilute than that approximately represented by the formula  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ .
- E. Attempts were made to obtain Weber's compound,  $\text{As}_2\text{O}_3 \cdot 6\text{SO}_3$  (see section 2), by recrystallising  $\text{As}_2\text{O}_3 \cdot 4\text{SO}_3$  (see B) from hot fuming acid containing so much sulphuric anhydride that it solidified on cooling; the product was not homogeneous; on one occasion, the crystals which separated appeared to be  $\text{As}_2\text{O}_3 \cdot 3\text{SO}_3$ ; but it is probable that the crystals were really a mixture. (The substance obtained gave 43.51 per cent.  $\text{As}_2\text{O}_3$ ; the compound  $\text{As}_2\text{O}_3 \cdot 3\text{SO}_3$  requires 45.21 per cent.  $\text{As}_2\text{O}_3$ ; the temperature required for solution was above the boiling point of sulphuric anhydride.)

5. The compounds obtained as described in 4 are very hygroscopic; they are decomposed by water, giving solutions containing sulphuric acid and arsenious oxide; those containing relatively much sulphuric anhydride ( $\text{As}_2\text{O}_3 \cdot 8\text{SO}_3$ , and  $\text{As}_2\text{O}_3 \cdot 4\text{SO}_3$ ) are separated into their constituent oxides below  $100^\circ$ ;  $\text{As}_2\text{O}_3 \cdot 2\text{SO}_3$  does not lose weight at  $150^\circ$ , but is completely decomposed at  $170^\circ$ ;  $\text{As}_2\text{O}_3 \cdot \text{SO}$  lost 5.4 per cent. by heating at  $225^\circ$  for four hours, the complete expulsion of all the sulphuric anhydride would have been attended

by a loss of 28.7 per cent.; the residue contained both arsenic and sulphur.

The compound  $\text{As}_2\text{O}_3 \cdot 3\text{SO}_3$  may be called the normal sulphate,  $\text{As}_2(\text{SO}_4)_3$ . This compound is less stable than either  $\text{As}_2\text{O}_3 \cdot 2\text{SO}_3$  or  $\text{As}_2\text{O}_3 \cdot \text{SO}_3$ ; it was obtained by Weber by dissolving  $\text{As}_2\text{O}_3$  in  $\text{SO}_3$  and distilling off the excess of the latter at a definite temperature; but it does not seem to have been certainly produced in any of the reactions described in this paper. Thus two specimens of  $\text{As}_2\text{O}_3 \cdot 4\text{SO}_3$  were re-crystallised from fuming acid, approximately  $3\text{H}_2\text{SO}_4 \cdot \text{SO}_3$ ; the results were as follow:—

	Percentage of $\text{As}_2\text{O}_3$ found.		Percentage of $\text{As}_2\text{O}_3$ calculated for
	Specimen I.	Specimen II.	
First crystallisation ..	55.37 p.c.	—	$\text{As}_2\text{O}_3 \cdot 6\text{SO}_3 = 29.20$ p. c.
Second „ ..	44.38 „	—	$\text{As}_2\text{O}_3 \cdot 4\text{SO}_3 = 38.22$ „
Third „ ..	37.79 „	64.80 p. c.	$\text{As}_2\text{O}_3 \cdot 3\text{SO}_3 = 45.21$ „
Fourth „ ..	60.67 „	56.24 „	$\text{As}_2\text{O}_3 \cdot 2\text{SO}_3 = 55.31$ „
			$\text{As}_2\text{O}_3 \cdot 6\text{SO}_3 = 71.22$ „

6. The method used for obtaining the various compounds described approximately pure and dry, namely, draining quickly and then pressing between dry porous tiles, was adopted, because the analytical results obtained from preparations which had remained over concentrated sulphuric acid were discordant. The comparative dryness of the porous tiles was found appreciably to affect the compositions of some of the compounds, especially when but a small quantity was at my disposal. The chief difficulty was to get the crystals quite free from adhering acid without decomposition by exposure to the air; the consequent uncertainty increased the experimental error.

The arsenic in the compounds described was estimated by titration with an iodine solution standardised against arsenious oxide. This method was found to give better results than that based on oxidation and estimation as magnesium pyroarsenate, with which I compared it in order to see whether any arsenic oxide had been formed by reduction of sulphuric anhydride. Sulphur trioxide was estimated as barium sulphate; the presence of considerable excess of hydrochloric acid, which was necessary to keep all barium arsenate in solution, possibly made the results slightly too low. Inasmuch as repeated estimations of both arsenious oxide and sulphuric anhydride showed that these two oxides were the only constituents of compounds prepared as described, it was deemed enough, as a general rule, to estimate one of the oxides only.

The following are the results of the analyses of the different compounds obtained (the reference letters correspond with those used in section 4):—

A.  $\text{As}_2\text{O}_3, 8\text{SO}_3$ . Analyses of five different preparations:—

	I.	II.	III.	IV.	V.
$\text{As}_2\text{O}_3$ . . . . .	22.41	24.2	21.27	24.29	22.95
$\text{SO}_3$ . . . . .	76.06	—	—	—	—

	Calculated for		
	$\text{As}_2\text{O}_3, 9\text{SO}_3$ .	$\text{As}_2\text{O}_3, 8\text{SO}_3$ .	$\text{As}_2\text{O}_3, 6\text{SO}_3$ .
$\text{As}_2\text{O}_3$ . . . . .	21.57	23.63	29.2
$\text{SO}_3$ . . . . .	78.43	76.37	70.8

B. (1)  $\text{As}_2\text{O}_3, 4\text{SO}_3$ . Analyses of two different preparations:—

	I.	II.	Calculated for $\text{As}_2\text{O}_3, 4\text{SO}_3$ .
$\text{As}_2\text{O}_3$ . . . . .	—	36.45	38.22
$\text{SO}_3$ . . . . .	61.01	—	61.78

(2)  $\text{As}_2\text{O}_3, 3\text{SO}_3$ ; from mother-liquor from above.

		Calculated for $\text{As}_2\text{O}_3, 3\text{SO}_3$ .
$\text{As}_2\text{O}_3$ . . . . .	43.99	45.21
$\text{SO}_3$ . . . . .	—	54.79

(3)  $\text{As}_2\text{O}_3, 2\text{SO}_3$ ; by recrystallising (2) from hot acid containing approximately 98 per cent.  $\text{H}_2\text{SO}_4$ .

	I.	II.	Calculated for $\text{As}_2\text{O}_3, 2\text{SO}_3$ .
$\text{As}_2\text{O}_3$ . . . . .	—	57.29	55.31
$\text{SO}_3$ . . . . .	45.33	—	44.69

(Mother-liquor from (3) gave crystals containing (a) 47.65, (b) 51.03 per cent.  $\text{SO}_3$ .)

C.  $\text{As}_2\text{O}_3, 2\text{SO}_3$ .

	I.	II.	III.	Calculated for $\text{As}_2\text{O}_3, 2\text{SO}_3$ .
$\text{As}_2\text{O}_3$ . . . . .	—	—	55.42	55.31
$\text{SO}_3$ . . . . .	41.08	44.19	—	44.69

D.  $\text{As}_2\text{O}_3, \text{SO}_3$ .

	From acid $9\text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$ .	From $9\text{H}_2\text{SO}_4, 4\text{H}_2\text{O}$ .	From $9\text{H}_2\text{SO}_4, 6\text{H}_2\text{O}$ .	From $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$ .
$\text{As}_2\text{O}_3$ . . . . .	70.65	72.21	—	70.99
$\text{SO}_3$ . . . . .	—	—	26.19	—

	Calculated for $\text{As}_2\text{O}_3 \cdot \text{SO}_3$ .
$\text{As}_2\text{O}_3$ .....	71.22
$\text{SO}_3$ .....	28.78

Solids which separated from acid, approximately  $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ , gave—

	I.	II.	III.
$\text{As}_2\text{O}_3$ .....	98.56	100.8	—
$\text{SO}_3$ .....	0.98	—	5.37

7. The results detailed in the preceding sections show that several definite but unstable compounds of arsenious oxide with sulphuric anhydride are produced by dissolving arsenious oxide in hot sulphuric acid of different concentrations, or in hot liquid sulphur trioxide, and allowing the liquid to cool. These compounds are  $\text{As}_2\text{O}_3 \cdot 8\text{SO}_3$ ,  $\text{As}_2\text{O}_3 \cdot 4\text{SO}_3$ ,  $\text{As}_2\text{O}_3 \cdot 2\text{SO}_3$ , and  $\text{As}_2\text{O}_3 \cdot \text{SO}_3$ . The compounds  $\text{As}_2\text{O}_3 \cdot 6\text{SO}_3$  and  $\text{As}_2\text{O}_3 \cdot 3\text{SO}_3$ , described by Weber (*vide* section 2), do not seem to be obtained by this method; to procure bodies of the compositions indicated by these formulæ, it is necessary to heat the oxides together, and then to distil off excess of sulphuric anhydride at definite temperatures.

There seems to be an upper and an under limit to the number of  $\text{SO}_3$  groups that can combine with  $\text{As}_2\text{O}_3$ ; when arsenious oxide is dissolved in excess of hot, liquid sulphuric anhydride, under increased pressure, the compound obtained on cooling is probably  $\text{As}_2\text{O}_3 \cdot 8\text{SO}_3$ ; when acid of the concentration approximately represented by the formula  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  is used, the compound obtained on cooling is  $\text{As}_2\text{O}_3 \cdot \text{SO}_3$ ; if the acid is more dilute than this, no compound of the two oxides is formed. When a considerable excess of arsenious oxide is dissolved in hot concentrated sulphuric acid, the excess of the oxide separates, on cooling, in combination with sulphuric anhydride, the quantity of which varies in accordance with the relative masses of the oxide and acid used; on agitating the mother-liquors, deposition of a definite compound occurs. On recrystallisation of the definite compounds from the same acids, the same phenomena are repeated. 100 grams of  $\text{H}_2\text{SO}_4$  can hold in solution and combination 1 gram of  $\text{As}_2\text{O}_3$ ; if there be more  $\text{As}_2\text{O}_3$  than this, the excess separates on cooling. As regards the action of heat, the most stable compound of the series examined is  $\text{As}_2\text{O}_3 \cdot \text{SO}_3$ ; this compound is probably partially volatilisable without decomposition. The variety and instability of the compounds described bears out the remark of Armstrong, that, in solution, like dissolves like; instead of the well-marked stable bodies which are produced by the combination of negative nitrous and sulphuric anhydride,  $\text{N}_2\text{O}_5 \cdot 2\text{SO}_3$ , or by the combination of positive

bismuthous oxide with the negative sulphuric anhydride,  $\text{Bi}_2\text{O}_3 \cdot 3\text{SO}_3$ , we have a series of bodies which are definite in composition, but have very little stability.

The compounds of arsenious oxide and sulphuric anhydride do not, I think, belong to the category of salts, understanding by this term the metallic derivatives of acids: the method of their production, and their instability towards sulphuric acid, water, and heat, points to a constitution analogous to that of the double salts. The compound  $\text{As}_2\text{O}_3 \cdot 3\text{SO}_3$ , the formula of which might be written  $\text{As}_2(\text{SO}_4)_3$ , is certainly quite as unstable as any of the others. I would regard them as composed of two radicles, both of which are negative, but one, of course, more negative than the other. These negative radicles combine in the ratio of one to one; but the compound thus formed is ready to take up a further quantity of the more negative radicle, and this further combination depends on the relative masses of the constituents of the reacting system, namely  $\text{As}_2\text{O}_3$ ,  $\text{H}_2\text{O}$ , and  $\text{SO}_3$ . As the quantity of the more negative radicle increases relatively to that of the less negative, the compounds become more unstable.

In the series of compounds we have another example of the shading off of chemical into physical action.

I must thank Mr. Pattison Muir for the use of his laboratory, and for kindly hints and assistance during the progress of the work. I hope, before long, to communicate to the Society an account of the compounds which antimonious oxide forms with sulphuric anhydride.

#### XXIV.—*The Vapour-density of Hydrogen Fluoride.*

By T. E. THORPE, F.R.S., and F. J. HAMELY.

IN a short paper published in the Transactions for 1888 (p. 765), we gave a preliminary account of an investigation which led us to conclude that the process of breaking up by heat of the molecular grouping of hydrogen fluoride in the state of vapour is analogous to that of acetic acid vapour, and that there was no evidence that a molecule corresponding to the formula of  $\text{H}_2\text{F}_2$  existed through any appreciable range of temperature. We now beg to lay before the Society a detailed account of the experiments by which we think this conclusion is substantiated.

The first attempt to determine the vapour-density of hydrogen fluoride was made by Gore (*Phil. Trans.*, 1869, 173). By heating a known volume of hydrogen with a slight excess of fused anhydrous

silver fluoride contained in a platinum vessel, Gore found that 1 vol. of hydrogen at about  $100^{\circ}$  became approximately 2 vols. of hydrogen fluoride at the same temperature, corresponding with the formula HF.

Mallet (*Amer. Chem. J.*, **3**, 89), in 1881, sought to determine the density by directly weighing the vapour in a vessel of known capacity. The hydrogen fluoride was prepared by heating cryolite with 100 per cent. sulphuric acid in a leaden retort, condensing the vapour in a leaden worm, and collecting the acid in a leaden bottle. Sufficient acid was prepared to produce at least eight times the volume of vapour required to fill the vessel employed. This was a large flask of Bohemian glass holding about  $4\frac{1}{2}$  litres, fitted with a cork carrying two tubes, one of which extended two-thirds within the body of the flask, whilst the other ended immediately below the cork. The flask, cork, and glass tubes were coated with paraffin melting at  $56^{\circ}$ , and the outer ends of the tubes could be closed by means of corks also coated with paraffin. The absolute weight, in a vacuum, of all the materials was determined. In the first experiment, the acid was volatilised at about  $25^{\circ}$  from the leaden tube, and was passed through a small glass tube coated with paraffin and containing phosphorus pentoxide; 4347.4 c.c. of vapour at  $29^{\circ}$  and 743.7 mm. were found to weigh 7.250 grams, whence the vapour-density is 21.06 ( $H = 1$ ). After its weight had been determined, the acid was absorbed by water and the solution tested: it was found to be free from silica, lead, sulphuric and sulphurous acids, but gave a reaction for phosphoric acid, due to the formation either of phosphorus pentafluoride or, more probably, of phosphoryl fluoride, by the action of the hydrogen fluoride on the phosphoric anhydride. Accordingly, in a second experiment, the phosphorus pentoxide was omitted, the upper end of the leaden worm being directly connected with the large flask, and a little of the 100 per cent. sulphuric acid was added to the liquid hydrofluoric acid in the leaden bottle whilst still in the freezing mixture. A new flask, fitted with tubes as in the first experiment, was used. 4394.7 c.c. of vapour at  $30.5^{\circ}$  and 745.2 mm. were found to weigh 6.819 grams, whence the vapour-density is 19.66 ( $H = 1$ ). Hence Mallet was apparently justified in assuming that the vapour-density of hydrogen fluoride at these temperatures corresponded with the formula  $H_2F_2$ , which by calculation gives the value 20.0 ( $H = 1$ ), whereas at  $100^{\circ}$  the density corresponded to HF. Mallet concludes his paper by a brief statement of the arguments in favour of the bivalent nature of fluorine as supported by his experiments, and points out how the constitution of a number of fluorine compounds may be conveniently exhibited on the supposition that fluorine has the same linking power as oxygen.

The only other observation of the kind of which we have been able



to discover any account was made by Vinzenz Kletzensky. In the obituary notice of this chemist given in the *Berichte der deutsch. chem. Gesell.* for 1882, p. 3312, there is an allusion to the results of experiments published in the *Jahresberichte der Handelsschule von Porques*, 1873, under the title "Ein Beitrag zur Chemie des Fluors," wherein the results of a vapour-density determination of hydrogen fluoride is given which led Kletzensky to the conclusion that fluorine is a bi-valent element. A reference is made to this estimation in the *Chemiker Zeitung* for 1884, p. 755, in a paper entitled "Die Fluormineralien," by Frhr. v. Jüptner, in which it is stated that Kletzensky found that the weight of 1 litre of hydrogen fluoride at 20° (30° ?) was from 1.75 to 1.79 grams, giving a molecular weight of about 39.5, and corresponding with  $\text{H}_2\text{F}_2$ .

It seemed to us important to study this question of the vapour-density of hydrofluoric acid in greater detail. The fact that hydrofluoric acid is liquid at the ordinary temperature, whereas its congeners, hydrochloric, hydrobromic, and hydriodic acids are only liquefied at very low temperatures, would seem to indicate a dissimilarity in molecular constitution as compared with these substances. Analogy would appear to show that, on the whole, the substance of lowest molecular weight should have the simplest constitution. Although water, which stands in the same relation to the hydrides of sulphur, selenium, and tellurium that hydrogen fluoride does to the hydrides of chlorine, bromine, and iodine, resembles hydrogen fluoride in being liquid at the ordinary temperature, there is, on the other hand, a striking point of difference between hydrogen fluoride and the other halogen hydrides, in the remarkable tendency to duplication of the fluorine compounds, as seen in the existence of the so-called acid fluorides, *e.g.*,  $\text{HKF}_2$  or  $\text{HF} \cdot \text{FK}$ , a fact which has been frequently noted, and which, many years ago, led to the suggestion that the true atomic weight of fluorine was 38—*i.e.*, twice its present value; and that hydrofluoric acid was in reality  $\left. \begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix} \right\} \text{f.}$  Gore, indeed, pointed out that hydrofluoric acid is by many of its properties placed between hydrochloric acid and water, but is much more closely allied to the former than to the latter. Hence, therefore, we thought it would be of interest to trace the process of breaking up of the complex molecule of the acid from temperatures close to its boiling point under ordinary pressures up to temperatures at which the density became normal. We might thereby hope to obtain not only additional material towards a discussion of the general theory of gaseous dissociation, but also to gain some information concerning the more strictly chemical question of the theory of definite valency.

It need hardly be pointed out that a research of this kind presents

certain special difficulties. Hydrofluoric acid is a disagreeable and, indeed, dangerous substance to work with, owing to its volatility and the extremely corrosive nature of its vapour. So energetically does it act on the membrane of the throat that an incautious inhalation of the vapour may produce temporary, and, as in the case of Knox, who attempted to electrolyse the acid, permanent loss of voice. Davy, for the same reason, was obliged to abandon his attempts to isolate fluorine. Louyet and Nicklès were killed by accidentally inhaling the vapour of the strong acid. A drop of it on the skin produces a very serious and painful wound, and even the vapour causes an intolerable pricking and burning sensation, which in one case within our knowledge was only relieved by lancing the finger at the place affected.

Moreover, in storing and using the anhydrous acid we are practically limited to vessels of platinum, since most of the lighter and cheaper metals are more or less acted upon by it. The anhydrous acid is said to have little or no action on dry glass, but it is so extremely hygroscopic that its indifference towards glass would be of doubtful practical benefit in such a matter as the determination of its vapour-density.

Hydrogen fluoride in the liquid state was first obtained by Fremy, by heating acid potassium fluoride, a method also followed by Gore (*loc. cit.*), who showed that the liquid boiled at about  $19^{\circ}$ , under ordinary atmospheric pressure. As this is still the most convenient mode of preparation for our purpose, we have employed it in much the same manner as adopted by Fremy and Gore.

*Preparation of Pure Aqueous Hydrofluoric Acid.*—Commercial redistilled hydrofluoric acid nearly always contains small quantities of sulphuric acid, notable quantities of sulphurous acid (from 1.5 to 2.0 per cent.), and occasionally large quantities of hydrofluosilicic acid. We found the best method of purification to consist in adding to the crude acid a strong solution of potassium permanganate, and thereafter potash, and to redistil from a platinum retort. The acid prepared in this way was found to be free from silica and sulphur acids, and to leave no residue on evaporation.

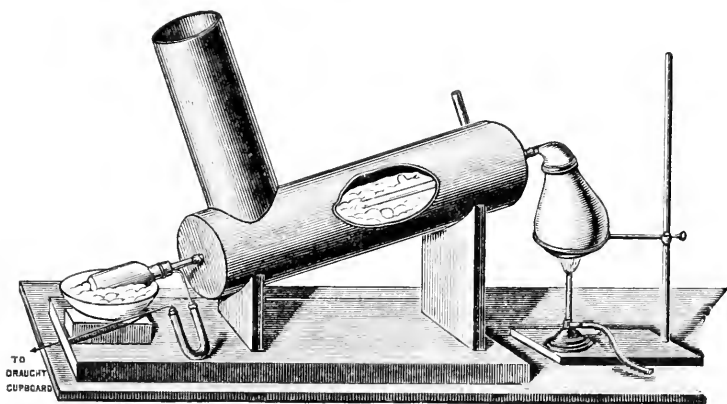
*Preparation of Acid Potassium Fluoride.*—This salt was prepared either by adding the theoretical quantity of pure potassium carbonate to the hydrofluoric acid (the strength of which had been ascertained by titration) in a large platinum dish and evaporating to dryness; or by adding the theoretical amount of aqueous acid to recently ignited potassium fluoride. In the first method the platinum dish was weighed, the aqueous acid poured into it, and the whole again weighed. The calculated amount of potassium carbonate was then added in small portions at a time, the solution

evaporated, and the whole heated until the salt fused to a thin, clear liquid, which on cooling solidified to a white, opaque, hard mass. If a slight excess of acid were used, the solid salt was less brittle and not perfectly opaque. The yield was in every case almost exactly that required by theory; thus, in one instance, 94 grams were obtained instead of 94.5; in another, 106.0 instead of 106.8 grams. The acid fluoride was powdered in a clean iron mortar and preserved in a leaden canister. Even after two months it showed no signs of having absorbed any very considerable quantity of moisture from the air.

The normal potassium fluoride, obtained by heating the acid salt to redness, is highly deliquescent. To convert it into the acid salt, it was strongly heated in a weighed platinum dish, quickly weighed when cold, and mixed with the theoretical quantity of pure hydrofluoric acid. The solution was evaporated to dryness and the residue heated as above described.

*Preparation of the Hydrogen Fluoride from the Acid Potassium Fluoride.*—The apparatus employed for this purpose is seen in Fig. 1; it differed but slightly from that used by Gore. The retort, condensing tube and receiver were made of platinum-iridium, the various

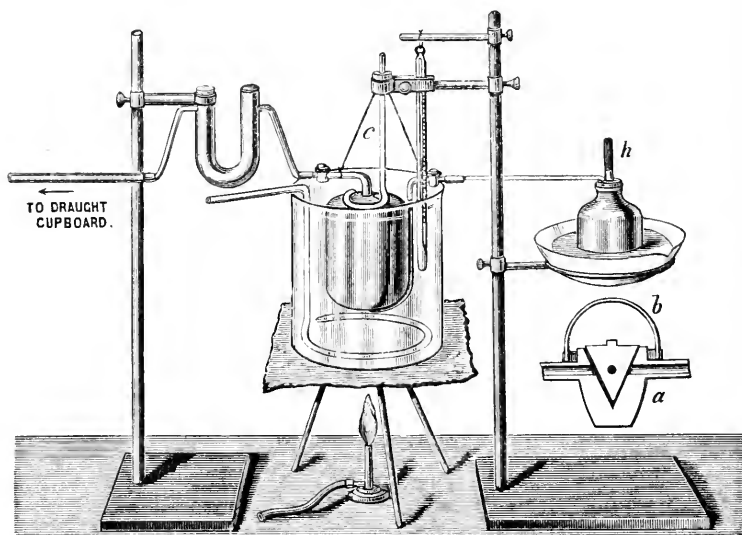
FIG. 1.



parts being fitted together by grinding. The retort was made in two pieces, the flanged upper part being connected with the body by a well-fitted joint. The condensing tube was 50 cm. long, tapering from 1.6 cm. to 0.6 cm. in diameter. The receiver was furnished with a carefully ground-in tubulated stopper, in addition to the solid one, through which was inserted the end of the condenser: into the tubulated stopper was soldered a short length of platinum tube 5 mm. in external diameter; this was connected with a leaden

U-tube containing a small quantity of oil of vitriol. The condensing tube, which was washed and ignited before each experiment, was fixed into the condenser by means of caoutchouc joints. The condenser was surrounded with a thick layer of flannel, and was filled with a mixture of ice and calcium chloride which gave an average temperature of  $-25^{\circ}$ , the receiver being also immersed in a similar mixture. After the receiver and tubulated stopper had been fixed to the condensing tube, the joint was covered with a thick layer of paraffin to prevent any condensed moisture from finding its way into the receiver. Before each preparation of hydrogen fluoride, a current of dry air was aspirated through the condensing tube, receiver, and leaden U-tube for about an hour. About 40 grams of the acid potassium fluoride, capable of yielding 11.5 litres of hydrogen fluoride at standard temperature and pressure, were used for each experiment, except in those cases where it was desired to obtain the vapour mixed with air (*v. infra*). The acid fluoride was placed in the open retort, melted and maintained in fusion for some little time to expel any hygroscopic moisture, the cap placed in position and in connection with the condenser, and the distillation proceeded with. When the bottom of the retort became red hot, the source of heat was removed, and the moisture condensed from the air on to the paraffined stopper was removed by blotting paper. The receiver was detached from the condensing tube, a wooden stopper covered with platinum foil (*h*, fig. 2) was inserted in the hole of the tubulated

FIG. 2.



stopper, and the receiver was connected with the tube of the platinum vessel in which the vapour was to be weighed, in the manner shown in Fig. 2, the dish supporting the receiver being meanwhile filled with ice-cold water.

*Mode of Determining the Vapour-density.*—The apparatus employed for this purpose is seen in Fig. 2. The vessel in which the vapour was weighed was constructed entirely of platinum, the tubes being connected with it by autogenous soldering, the two stopcocks being fastened to the tubes by gold-solder. The stopcocks (see *a*, Fig. 2) are made of solid platinum, as also are the cones which are ground into them. The upper part of the stopcocks is made cylindrical in order that a glass cap, *b*, might be fitted air-tight upon it by means of a caoutchouc ring. The cones were most carefully ground in, and the cocks were found to be tight even under considerably reduced pressures and at temperatures beyond that at which the vapour-density of hydrogen fluoride becomes normal.\* The cones were covered with a thin film of vaseline (upon which hydrogen fluoride has no perceptible action) before inserting them; at the higher temperatures, we used a mixture of vaseline and anthracene made by rubbing the two substances together in a mortar.

Three determinations of the capacity of the vessel up to the stopcocks, at 0° C., made by filling it with distilled water at a known temperature, gave respectively—

(1) .....	288·61 c.c.
(2) .....	288·54 „
(3) .....	288·65 „
Mean ....	<hr/> 288·60 „

Another experiment made when the vessel had been in use for some time, and when from the soft and yielding character of the metal it might be supposed that its shape might possibly have altered, gave 288·57 c.c.

Before connecting it with the receiver containing the liquid hydrogen fluoride, the vessel was carefully rinsed with distilled water and heated over a Bunsen flame whilst a current of dry air was drawn through it. When cold, the cones were lightly touched with vaseline, the caps fixed in position, and the whole placed in the balance case, one cock being open in order to equalise the pressure, and weighed after standing for about 40 minutes, the temperature and pressure being noted at the time. The glass caps were then removed, and a piece of cardboard was fastened by wire below the

\* Our thanks are due to Messrs. Johnson, Matthey & Co., for the care with which this very essential portion of the apparatus was constructed.

stopcocks in order to prevent any possible splashing on to them from the heated glycerol-bath in which the vessel was placed. The vessel was next attached to the clamp, and the curved glass tube, *c*, adjusted so as to keep it in position. It was now lowered into the bath previously heated to the desired temperature, the platinum U-tube containing a small quantity of concentrated sulphuric acid was next attached, from which was a long length of thin leaden tube leading to the draught place. A current of dry air was then drawn through the entire system. The platinum receiver was next joined to the vessel, and the ice was removed from the dish, which was then filled with water at about 25°. The hydrogen fluoride rapidly volatilised and expelled the dry air from the vessel, and the passage of the air-bubbles could be traced by the slight vibration of the platinum U-tube. When the hydrogen fluoride reached the oil of vitriol, the liquid became hot, possibly from the formation of fluosulphonic acid.

As soon as the vaporisation, which always took place at a temperature not exceeding 30°, was complete, the cocks were closed, the U-tube and receiver were removed, and the bath was stirred for some little time to equalise its temperature throughout. One of the cocks was then momentarily opened, the temperature of the bath and the barometric height noted, the cardboard removed, the glass caps replaced, the vessel withdrawn from the bath and washed with distilled water; after being dried, it was placed in the balance case, and, after standing for about 40 minutes, reweighed.

*Determination of the Amount of Residual Air.*—After the vessel filled with vapour had been weighed, the caps were removed, and the whole was immersed in distilled water; the cock of the tube leading to the bottom of the vessel was then opened and the water allowed to rush in. The water in the bath was stirred, the temperature noted, and the platinum vessel raised until the open cock was close to the surface, when the cock was turned. The platinum vessel after being wiped dry was again weighed.

*Reduction of the Observations.*—Corrections have been made in each experiment for the expansion of the platinum vessel, specific gravity of water weighed, and its loss of weight in air. No corrections have been made for (1) the change in buoyancy of the air from variations in temperature and pressure between the weighing of the bulb and air, and the weighing of the bulb and vapour; (2) the aqueous vapour in the air at the first weighing; (3) the possible solution of residual air in the water used for absorbing the vapour (as the distilled water employed was probably nearly saturated with air, this correction must be practically nil); (4) the varying height of the barometric column due to temperature corrections. 2 and 4 act in opposite directions, and nearly eliminate each other under ordinary conditions.

The following is an example of the mode of calculation:—

Capacity of bulb at  $0^{\circ} = 288.6$  c.c.

Weight of 1 c.c. of air at  $0^{\circ}$  and 760 mm. = 0.0012928 gram.

Cubical expansion of Pt for  $1^{\circ}$  C. = 0.000027.

Thermometer in melting ice registers  $+0.5^{\circ}$ .

„ at 760 mm. tension registers  $100.7^{\circ}$ .

Sp. gr. of air ( $H = 1$ ) = 1.435.

*Expt. No. 43 (under Diminished Pressure).*

Wt. of bulb + caps in air at  $19.7^{\circ}$  C. and 772 mm. = 244.0120 grams.

Wt. of bulb + caps + vapour (in air at  $17.5^{\circ}$  C. and 772 mm.) = 244.0025 grams.

Cocks turned off at  $31.8^{\circ}$  C.

Barometer 772.3 mm.; manometer reading = 106.2 mm.

Pressure =  $772.3 - 106.2 = 666.1$  mm.

Wt. of bulb + caps + water at  $24.3^{\circ}$  C. = 528.18 grams.

(1.) Wt. of air in bulb at first weighing—

$$= \frac{0.0012928 \times 288.6 (1 + 0.000027 \times 19.7) 772}{(1 + 0.003665 \times 19.7) 760} = 0.3537.$$

(2.) Wt. of bulb + air..... 244.0120 grams.

Wt. of air (1)..... 0.3537 „

Wt. of vacuous bulb in air ..... 243.6583 „

Wt. of bulb + vapour ..... 244.0025 „

Wt. of vacuous bulb ..... 243.6583 „

Wt. of vapour + residual air ..... 0.3442 „

(3.) Cocks were closed at  $31.8^{\circ}$  and 666.1 mm.

Volume of vapour + residual air at  $0^{\circ}$  and 760 mm.—

$$= \frac{288.6 (1 + 0.000027 \times 31.8) 666.1}{(1 + 0.003665 \times 31.8) 760} = 226.69 \text{ c.c.}$$

(4.) Residual air—

Wt. of bulb + water at  $24.3^{\circ}$  ..... 528.18 grams.

Wt. of bulb + air at  $19.7^{\circ}$  and 772 mm. 244.01 „

(Residual air about 3.6 c.c. = 0.005).. 284.17

Approximate weight of dissolved HF . 0.34

Wt. of  $H_2O$  — wt. of same vol. of air.. 283.83

283.83

Sp. gr.  $\text{H}_2\text{O}$  at  $24.3^\circ$  — sp. gr. air at  $19.7^\circ$  and 772 mm.  
 = 284.95 c.c. water at  $24.3^\circ$ .

Residual air at  $0^\circ$  and 760 mm.—

$$= \frac{\{288.6 (1 + 0.000027 \times 24.3) - 284.95\} 772}{(1 + 0.003665 \times 24.3) 760} = 3.58 \text{ c.c.}$$

$$3.58 \times 0.0012928 = 0.0046 \text{ gram.}$$

$$\text{Per cent. residual air} = \frac{3.58 \times 100}{226.69} = 1.58 \text{ per cent.}$$

$$\text{Per cent. vapour} = 98.42 \text{ per cent.}$$

$$\text{Actual pressure of vapour} = 666 \times 0.9842 = 655 \text{ mm.}$$

(5.)

$$(2) \text{ Wt. of vapour + air } \dots \quad 0.3442 \text{ gram.}$$

$$(4) \text{ Wt. of air } \dots \dots \dots \quad 0.0046 \quad , ,$$

$$\text{Wt. of vapour } \dots \dots \dots \quad 0.3396 \quad "$$

$$(3) \text{ Vol. of vapour + air } \dots \quad 226.69 \text{ c.c.}$$

$$(4) \text{ Vol. of air } \dots \dots \dots \quad 3.58 \quad , ,$$

$$\text{Vol. of vapour } \dots \dots \dots \quad 223.11 \quad , ,$$

$$\text{V.-D. (Air} = 1) = \frac{0.3396}{223.11 \times 0.0012928} = 1.177$$

$$\text{V.-D. (H} = 1) = \frac{0.3396}{223.11 \times 0.000089578} = 16.99$$

$$\text{Mol. wt.} = 1.177 \times 28.87 = 33.99.$$

A series of experiments was made in this manner at temperatures varying between  $26.4^\circ$ , that is, about  $7^\circ$  above the boiling point of liquid hydrogen fluoride under ordinary atmospheric pressure, and  $88.1^\circ$ . The results are shown in Table I.

TABLE I.—*Showing Vapour-density of Hydrogen Fluoride at Temperatures varying between  $26.4^\circ$  and  $88.1^\circ$ .*

	Theoretical vapour-density.	
	Air = 1.	H = 1.
$\text{H}_3\text{F}_3$ .....	2.0781	30.0
$\text{H}_2\text{F}_2$ .....	1.3854	20.0
$\text{HF}$ .....	0.6927	10.0



TABLE I.

No. of expt.	Temp. °C.	Barometer at time of expt.	Per cent. of residual air.	Pressure of vapour.	V.-D. air = 1.	V.-D. H = 1.	Mol. wt.
2	26·4	756	1·51	745	1·773	25·59	51·18
21	27·8	763	2·23	746	1·712	24·71	49·42
7	29·2	762	1·55	750	1·578	22·77	45·54
19	32·0	754·5	1·52	743	1·377	19·87	39·74
4	33·1	770·5	2·64	750	1·321	19·06	38·12
5	33·8	767	1·14	758	1·270	18·33	36·66
18	36·3	751	1·58	739	1·115	16·10	32·20
8	38·7	764	1·69	751	1·021	14·73	29·46
9	39·2	759	2·08	743	1·002	14·47	28·94
10	42·8	767·5	3·42	741	0·910	13·13	26·26
11	47·3	766	2·76	745	0·823	11·88	23·76
12	57·5	760	1·36	750	0·737	10·64	21·28
13	69·4	764	2·37	746	0·726	10·48	20·96
16	88·1	753·5	1·65	741	0·713	10·29	20·58

These observations are graphically represented in Fig. 3 (p. 174). Strictly speaking, they ought to be reduced to a common pressure; they may, however, be considered, without sensible error, as referred to the average pressure of 746 mm.\*

A glance at the numbers, and more especially at the curve, at once shows that the process of dissociation of the vapour of hydrogen fluoride is a perfectly continuous one, and that there is no direct evidence of the existence of a molecule corresponding to the formula  $\text{H}_2\text{F}_2$ . If such a molecule exists, it must be formed only during the process of transition of  $\text{H}_x\text{F}_x$  molecules, and be such that it can persist under given circumstances only in the presence of definite proportions of molecules more and less complex than itself. The density at about  $32^\circ$  corresponds apparently with  $\text{H}_2\text{F}_2$ , but the curve gives no indication of any condition of statical equilibrium in the neighbourhood of this temperature such as would be manifest if such

\* Influence of possible errors of observation upon the result.

Expt. 19. V.-D. 1·377 at  $32\cdot0^\circ\text{C}$ . and 743 mm.

Difference of 1 mm. in *all* the barometric readings affects the result by 0·0005.

Difference of 1 mm. in the reading of the barometer, at time of turning off cock, by 0·0017.

Difference of  $1^\circ\text{C}$ . in reading temperature of bath, by 0·004.

Difference of 0·001 gram in the weighings by 0·003.

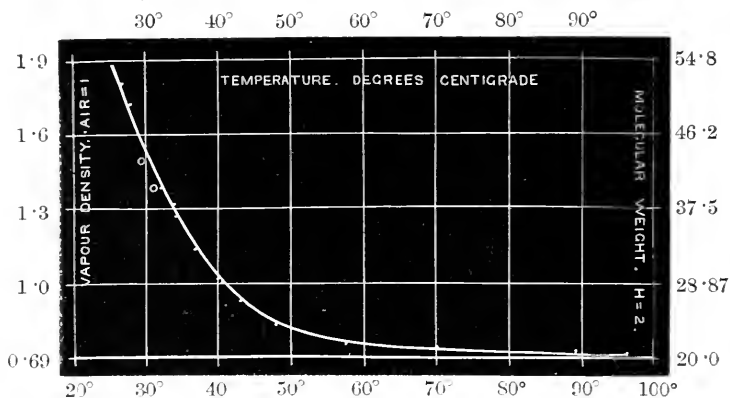
Expt. 42. V.-D. 0·789 at  $32\cdot3^\circ\text{C}$ . and 353 mm. (diminished pressure).

Difference of 1 mm. in reading of manometer, by 0·002.

Difference of  $1^\circ\text{C}$ . in reading temperature of bath, by 0·003.

Difference of 0·001 gram in the weighings, by 0·007.

FIG. 3.—Vapour-density of Hydrogen Fluoride at varying Temperatures.



a molecule were capable of independent existence. At temperatures below this point, the vapour-density gradually increases in a regular manner until at  $26.4^{\circ}$ , the lowest temperature observed, the vapour-density becomes 1.773, equivalent to a molecular weight of 51.2 ( $\text{H}_3\text{F}_3 = 60$ ); as it is heated, the vapour behaves like a mixture of a complex molecule  $\text{H}_x\text{F}_x$ , or of  $\text{H}_x\text{F}_x$  and  $\text{H}_y\text{F}_y$  molecules, with a gradually increasing number of molecules of  $\text{HF}$ , the process of dissociation being perfectly continuous until the temperature increases to about  $60^{\circ}$ , when the density becomes approximately normal, that is, corresponds to a vapour consisting wholly of  $\text{HF}$  molecules.

On comparing Mallet's values with those obtained by us, it will be seen that his numbers lie very nearly upon the curve above given. As it happens, the pressure at which his observations were made is almost exactly the mean pressure in our experiments. Mallet's numbers reduced to air as unity are respectively 1.459 at  $29^{\circ}$  and 1.363 at  $30.5^{\circ}$ . These values are indicated by the small circles on the diagram. The divergences from our curve are such as might be caused by a difference of about  $1^{\circ}$  C. in the temperature of the vapour, and as Mallet employed upwards of  $4\frac{1}{2}$  litres of vapour—whereas the volume in our experiments was less than 300 c.c., such a difference might well exist, especially when we bear in mind that a considerable amount of heat must be absorbed in the conversion of the complex molecules into the more simple ones. Moreover, it must not be forgotten, as Willard Gibbs has already pointed out, that when the density varies rapidly with the temperature, determinations of density for the same temperature and pressure by different observers, or different determinations by the same observer, exhibit discordances which are of an entirely different order of magnitude from those

which occur with substances of normal or constant densities, or which occur with the same substance at temperatures at which the density approaches a constant value. In any case, the variation is sufficiently small to show that the material of the vessel has no very sensible influence on the result, and that there is no tendency to occlusion or condensation on the platinum. This fact is of some importance, since Konowaloff (*Ber.*, **17**, 1361, and **18**, 2808) has offered some experimental evidence to show that in the case of the tertiary amyl acetate and chloride, normal propyl and isopropyl bromides, formic acid and other substances, the nature of the vessel exerts a very considerable influence on the rate and extent of the dissociative change, due possibly to the effect of surface-tension (compare, however, V. Meyer and Pond, *Ber.*, **18**, 1623).

Dissociation-curves are of two kinds. The first type is that exhibited by the well-known case of amylene hydrobromide, in which the density of the vapour remains constant within certain limits of temperature, and then begins to decrease as the temperature rises, at first slowly, then more rapidly, and then again slowly, until at a certain temperature the vapour-density once more became constant, and in this special case the final constant value is exactly half of the initial constant value.

This particular character of the change has been noticed in many instances, but it has only been carefully studied in comparatively few, the best known of which is nitrogen peroxide. In that case, the process of decomposition is generally regarded as the resolution of  $\text{N}_2\text{O}_4$  mols. into molecules of  $\text{NO}_2$ ; and on this assumption the percentage decomposition at each particular stage of temperature can be calculated on the basis of Avogadro's hypothesis. A curve showing the increase of dissociation for a given increment in temperature is perfectly symmetrical: it gradually rises to a maximum, and then as gradually descends to a minimum. E. and L. Natanson (Wiedemann, *Ann. Phys. Chem.*, **24**, 454) have determined the relation of the specific heats at constant pressure and at constant volume of nitrogen peroxide at different stages of the dissociative change by Kundt's method, with the object of obtaining evidence as to the molecular constitution of the gas at different temperatures; and the result of this work tends to show that the change consists in the transformation of  $\text{N}_2\text{O}_4$  molecules into  $\text{NO}_2$ , and that it is not, as Deville declared, and as Berthelot, Troost, and Lemoine still maintain, dependent upon any variation from the laws of Boyle and Gay-Lussac, exhibited by the vapour. Further evidence that nitrogen peroxide is actually  $\text{N}_2\text{O}_4$ , even in the liquid state, is afforded by the experiments by Raoult's method of Professors Ramsay and Young (*Trans.*, 1888, 622). They have shown that the depression in the melting point of

acetic acid by the addition of nitrogen peroxide corresponds to a molecular weight of 92, and hence, therefore, to the formula  $N_2O_4$  (see also Ramsay and Young, *Phil. Mag.*, Feb., 1887).

Now, when we apply these considerations to the case of hydrogen fluoride, we are met with the difficulty that we have no knowledge of the molecular constitution of the vapour below the temperature at which the density becomes normal. It is obvious that the change cannot be solely attributed to a resolution of  $H_2F_2$  molecules into HF molecules. Nor, unless there is a turning point in the curve at temperatures below  $25^\circ$ , analogous to that observed in the case of amylene hydrobromide, can we definitely conclude that the molecule at the lower temperatures is  $H_3F_3$ . The existence of the acid fluoride,  $KF, HF$ , which has been written  $KF-FH$ , has been held to justify the supposition that  $HF-FH$  also exists. But Moissan (*Compt. rend.*, 106, 547—549) has shown that hydrofluorides of potassium fluoride of the formulæ  $KF, 2HF$  and  $KF, 3HF$  may be obtained, and these may equally be held to justify the supposition that the molecules  $H_4F_4$  and  $H_3F_3$  also exist. The former compound is stable only at low temperatures; the latter may be heated to its liquefying point, viz.,  $105^\circ$ , without decomposition. These compounds are strictly analogous to the hydrochlorides of chlorides of gold, platinum, mercury, and cadmium, and to the hydrochlorides of zinc chloride,  $ZnCl_2, HCl$  and  $(ZnCl_2)_2, HCl$ , described by Engel (*Ann. Chim. Phys.* [6], 1887, 10, 424). But the existence of these substances has not usually been regarded as justifying the polyvalent character of chlorine. Hence, therefore, the argument as to the bivalent or, indeed, polyvalent character of fluorine seems to us to be inconclusive.

It would have been interesting, no doubt, to have made determinations at temperatures even closer to the boiling point than we have actually done, but the experimental difficulties in the way of such determinations are very considerable; a very slight reduction in the temperature of such parts of the apparatus as were necessarily outside the bath might at temperatures so near the condensing point of the hydrogen fluoride, occasion very serious errors. They might, in fact, have occasioned an apparent turning point in the curve when no such discontinuity in reality existed.

Extrapolation is of course always hazardous; but if the direction of the curve of vapour-density (Fig. 3) be prolonged from  $25^\circ$  to  $19^\circ$ —that is, to the boiling point of the hydrogen fluoride, the calculated molecular weight of the vapour at the latter temperature approximates to a value between  $H_4F_4$  and  $H_3F_3$ . Now, assuming Naumann's theory of dissociation to be valid, it may be worth while to trace the dissociative change, on the supposition that it consists of the resolution of either  $H_4F_4$  or  $H_3F_3$  molecules into HF molecules.

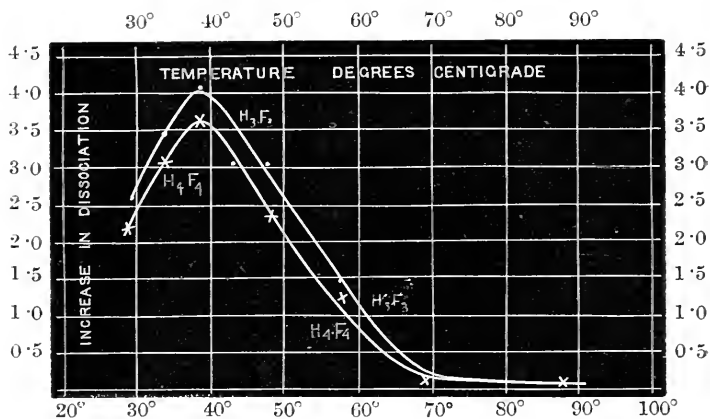
The following table shows the observed density of the hydrogen fluoride at the various temperatures; the percentage decomposition of the  $\text{H}_4\text{F}_4$  and  $\text{H}_3\text{F}_3$  molecules at that temperature calculated by the well-known formula  $\frac{D-D'}{(n-1)D'}$ , and the mean increase of dissociation for  $1^\circ \text{C.}$  over intervals of above  $5^\circ$  up to the temperature  $42.8^\circ$ , and thereafter over the intervals of the individual experiments.

TABLE II.

$^\circ \text{C.}$	Density.	Percentage decomposition.		Mean increase for $1^\circ \text{C.}$	
		$\text{H}_4\text{F}_4$ .	$\text{H}_3\text{F}_3$ .	$\text{H}_4\text{F}_4$ .	$\text{H}_3\text{F}_3$ .
		per cent.	per cent.	per cent.	per cent.
26.4	1.773	18.76	8.60	—	—
27.8	1.712	20.63	10.69	—	—
29.2	1.578	25.20	15.84	2.30	2.60
32.0	1.377	33.75	25.45	—	—
33.1	1.321	36.59	28.65	—	—
33.8	1.270	39.41	31.81	3.09	3.47
36.3	1.115	49.52	43.19	—	—
38.7	1.021	57.14	51.77	3.62	4.07
39.2	1.002	58.86	53.71	—	—
42.8	0.910	68.17	64.19	2.70	3.03
47.3	0.823	78.91	76.25	2.39	2.68
57.5	0.737	91.98	90.97	1.28	1.44
69.4	0.726	93.91	93.11	0.16	0.18
88.1	0.713	96.23	95.72	0.12	0.14

The main result of this table is to bring out the fact that, as in the case of nitrogen peroxide, the increase of dissociation becomes greater and greater as the temperature increases, until it obtains its maximum when about 50 per cent. of the heavier molecules have been decomposed, after which the increase becomes gradually smaller, at first slowly, and then rapidly. The curves showing the mean increase (Fig. 4, p. 178) resemble, in fact, that given by Naumann (*Thermochemie*, 1882, 1171) in order to represent the increase in the rate of dissociation of nitrogen peroxide, but with this very marked difference, that the mean increase for  $1^\circ \text{C.}$  in the case of hydrogen fluoride is at its maximum nearly three times as great as that of nitrogen peroxide.

But the general character of the dissociation-curve of hydrogen fluoride (Fig. 3) more nearly resembles that of the second type. It has, indeed, the closest analogy to the dissociation-curve of acetic acid, except that in the case of hydrogen fluoride the process of molecular breaking down is effected over a much shorter interval of tem-

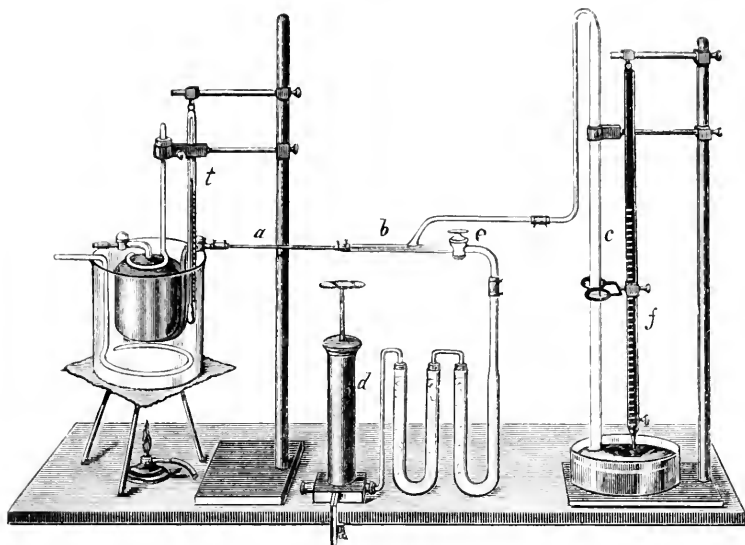
FIG. 4.—Curves showing mean amount of dissociation for  $1^\circ \text{C.}$  at varying temperatures, and at 760 mm. pressure.

perature. As to the nature of the molecular groupings in acetic acid vapour below  $250^\circ$ , at which temperature the density first appears, under ordinary atmospheric pressures, to correspond with  $\text{C}_2\text{H}_4\text{O}_2$ , we have no more knowledge than in the case of hydrogen fluoride. All we know is that at the lower temperature the density approximates to a molecular weight corresponding with  $\text{C}_4\text{H}_8\text{O}_4$  and Horstmann (*Annalen*, Suppl. 6, 53) has suggested that the existence of the acid potassium acetate,  $\text{KC}_4\text{H}_8\text{O}_4$  or  $\text{C}_2\text{H}_4\text{O}_2 \cdot \text{C}_2\text{H}_3\text{KO}_2$ , may be held to indicate that such a duplication of the ordinary molecule in the gaseous state can take place, exactly as the existence of the acid potassium fluoride,  $\text{KF} \cdot \text{FH}$ , has been regarded as evidence of the existence of  $\text{H}_2\text{F}_2$ . It must, however, be admitted that the argument has no greater weight in the one instance than in the other (see, however, Ramsay and Young, *loc. cit.*).

It is well known that in all these cases the extent of the dissociation corresponding to any given temperature is greatly augmented by reduction of pressure. We have accordingly made a series of observations of the vapour-density of hydrogen fluoride at a given temperature under varying pressures. The apparatus we have employed for this purpose is seen in Fig. 5.

The platinum vessel, after having been filled with hydrogen fluoride in the manner already described, was attached by means of a short length of narrow leaden tubing *a* to the glass tube *b* which, in its turn, was connected with the manometer *c*, and the exhausting syringe *d*. The glass tube was provided with a stopcock, and between the end of the tube and the syringe were two U-tubes filled

FIG. 5.



with soda-lime. The various parts of the glass, as also the rubber corks and joints, were carefully coated with paraffin. The glycerol bath having been brought to the constant temperature, and maintained at that point for some time, the exhausting syringe was worked until the mercury in the manometer stood at some little distance above the desired pressure, when the glass stopcock *c* was closed and the stopcock of the platinum apparatus cautiously opened; the alternate opening and closing and occasional working of the syringe being repeated until the desired reduction of pressure was effected. Repeated observation showed that the molecular breaking down of the enclosed hydrogen fluoride is not absolutely instantaneous; but great care was taken to ensure that the volume of the hydrogen fluoride showed no further alteration; in all cases both temperature and pressure became eventually constant, and remained so for some time before the final readings on the attached millimetre scale *f* and thermometer *t* were taken. The apparatus was then weighed, and the amount of the residual air determined in the manner already described. The results are seen in Table III (p. 180).

These results are graphically represented in Fig. 7, p. 182.

It will be at once evident why the particular temperature of about  $32^{\circ}$  was selected. It is at this point that the vapour of hydrogen fluoride is supposed to consist wholly of  $\text{H}_2\text{F}_2$  molecules. It will be seen, however, that the slightest alteration of pressure at this tem-

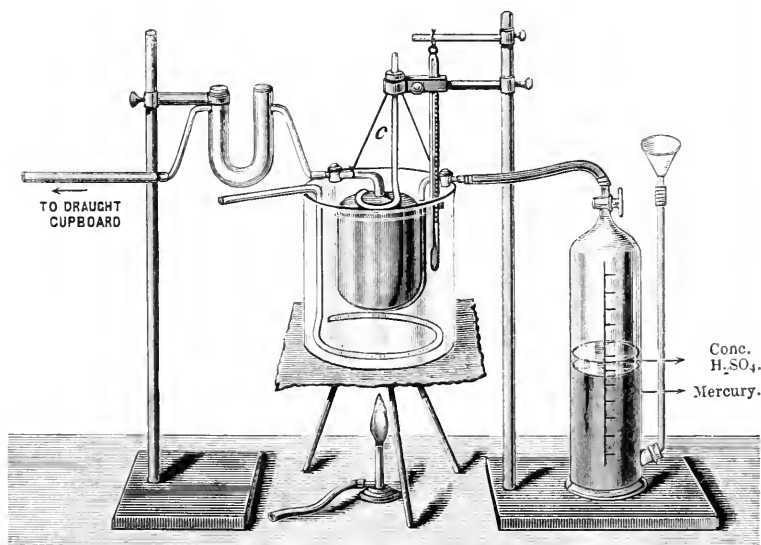
TABLE III.—*Showing Vapour-density of Hydrogen Fluoride under varying Pressures and at a constant Temperature (31·8—32·5°).*

No. of expt.	° C.	Mano- meter.	Per cent. of residual air.	Partial pressure.	V.-D. Air = 1.	V.-D. H = 1.	Mol. wt.
19....	32·0	754·5	1·52	743	1·377	19·87	39·74
41....	32·2	703·0	2·35	686	1·239	17·89	35·78
43....	31·8	666·0	1·58	655	1·177	16·99	33·98
41....	32·0	613·0	1·68	603	1·068	15·41	30·82
40....	32·5	570·0	4·45	545	0·963	13·89	27·78
39....	32·3	511·0	2·45	498	0·920	13·27	26·54
45....	31·9	371·0	4·65	354	0·797	11·50	23·00
42....	32·3	372·0	5·21	353	0·789	11·39	22·78

perature at once disturbs the ultimate proportion of the complex to the simpler molecules in the gaseous mixture, and accordingly there is here no evidence of the existence of a stable molecule corresponding to  $\text{H}_2\text{F}_2$ .

The reduction of the actual pressure may, however, be effected by diluting the hydrogen fluoride with an indifferent gas, as, for example, dry air. We have accordingly made a series of experiments at a constant temperature (about 32°) and at atmospheric pressure, by

FIG. 6.





diluting the hydrogen fluoride with air, weighing the mixture, and determining the amount of admixed air in the manner already described. The platinum vessel was first filled with hydrogen fluoride in the usual manner, and air, dried by long contact with oil of vitriol, was passed into the apparatus from the graduated reservoir (Fig. 6). It was of course necessary to pass a greater quantity of air into the platinum vessel than was ultimately found there. After passing the air into the bulb, the U-tube and air reservoir were removed and the bath kept at the constant temperature for about half an hour before finally equalising the pressure in the bulb. In determining the residual air, the vessel was left under water for at least 30 minutes, the cock being occasionally turned off and the vessel briskly shaken.

The numerical details of this series of experiments are given in Table IV.

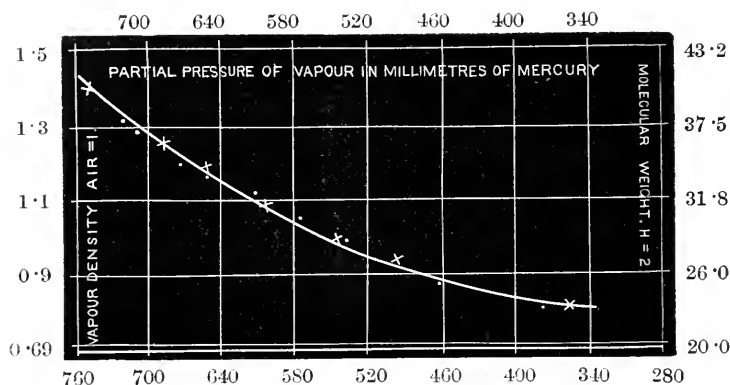
TABLE IV.—*Showing the Vapour-density of Hydrogen Fluoride at about 32° when mixed with varying Quantities of Air.*

No. of expt.	Temp. ° C.	Barometer at time of expt.	Per cent. of residual air.	Partial pressure of vapour.	V.-D. Air = 1.	V.-D. H = 1.	Mol. wt.
19	32·0	754·5	1·52	743	1·377	19·87	39·74
6	31·7	757·5	4·57	723	1·309	18·90	37·80
23	31·8	765·0	6·94	712	1·290	18·62	37·24
3	32·5	772·0	12·59	675	1·182	17·05	34·10
24	31·7	769·0	20·59	611	1·102	15·91	31·82
27	31·7	762·0	24·62	574	1·035	14·94	29·88
29	31·7	750·0	28·15	539	0·967	13·96	27·92
31	31·6	762·0	39·25	463	0·854	12·32	24·64
30	31·5	744·0	49·58	375	0·785	11·33	22·66

A graphical representation of these results is seen in Fig. 7. The temperature of about 32° was selected with the view of seeing if the intervention of the air particles made any difference in the amount of dissociation. The character of the curve representing the decrease in density by direct diminution of pressure—that is, by the use of the exhausting syringe, is identical with that given by mixing the vapour with air. The results given in Table III are indicated in Fig. 7 by the crosses: it will be seen that they lie practically on the curve. Hence it would appear that the intervention of the air particles has no effect on the extent of the ultimate molecular breaking down of the hydrogen fluoride molecules corresponding to a particular diminution of pressure. The presence of the air may alter the rate of the dissociation, but it would seem to have no appreciable influence on its amount.

FIG. 7.—Results obtained with Diminished Pressures at Temperatures between  $31\cdot5^{\circ}$  and  $32\cdot5^{\circ}$  C.

Results marked  $\times$  diminution of pressure obtained directly.  
Results marked . by mixing vapour with air.



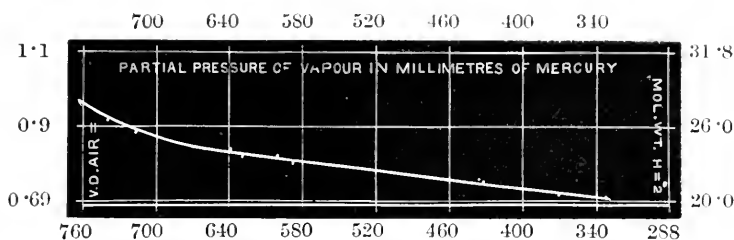
We have thought it would be of interest to trace the dissociative change consequent on reduction of pressure at another temperature, and we have accordingly made a series of experiments at a temperature of about  $42\cdot5^{\circ}$  with gradually increasing quantities of admixed air. The results are seen in Table V.

TABLE V.—*Showing the Vapour-density of Hydrogen Fluoride at about  $42\cdot5^{\circ}$  when mixed with varying Quantities of Air.*

No. of expt.	Temp. $^{\circ}$ C.	Baro- meter.	Per cent. of residual air.	Partial pressure.	V.-D. Air = 1.	V.-D. H = 1.	Mol. wt.
10	42.8	767.5	3.42	741	0.910	13.13	26.26
37	42.1	759.0	5.39	718	0.877	12.65	25.30
35	42.2	773.0	17.18	640	0.814	11.74	23.48
36	42.2	770.0	18.01	631	0.813	11.73	23.46
34	42.0	770.0	21.98	601	0.802	11.57	23.14
32	42.0	765.0	22.96	589	0.784	11.32	22.64
38	42.4	750.0	42.07	434	0.745	10.75	21.50
33	42.5	762.0	51.38	370	0.704	10.16	20.32

Fig. 8 gives a graphical representation of the change; as might be expected, the decrease in density for a given alteration in pressure is much less at  $42\cdot5^{\circ}$  than at  $32^{\circ}$ , and the curve in the former case more nearly approximates to a straight line.

FIG. 8.—Results obtained by mixing the Vapour with Air at Temperatures between 42·0° and 42·8° C.



Formulae connecting the vapour-density of a dissociable gas with its temperature and pressure, based on thermodynamical considerations, have been constructed independently by Willard Gibbs (*Amer. J., Sci.*, 1879; *Chem. News*, 1879, 222), Boltzmann (*Wied. Ann.*, 22, 39), and J. J. Thomson ("Applications of Dynamics to Physics and Chemistry," *Macmillans*, 200). These formulae have hitherto had reference to the cases of substances like nitrogen peroxide, acetic acid, and formic acid, where a molecule of the substance in the initial state is held to dissociate into two molecules of the same kind, or into two molecules occupying the same volume. In the case of hydrogen fluoride, the changing system is probably more complex, and if we assume the initial state to correspond with  $\text{H}_2\text{F}_4$ , we may have mixtures of molecules of all intermediate values down to  $\text{HF}$ . In such cases, the mathematical expressions in their original form are no longer applicable.

The formula—

$$\log \frac{D_1^3(D - D_1)}{p^3(4D_1 - D)^4} = -A' - B' \log t + \frac{C}{t},$$

in which

$$\begin{aligned} D_1 &= 0.693 \\ A' &= 2178.1047 \\ B' &= -729.7222 \\ C &= 108409.9 \end{aligned}$$

reproduces the values in Series I with an average error of from 0.01 to 0.02, but in the cases of Series IV the values obtained from the equation are much further from those of observation.

It has already been stated that a prolongation of the curve in Fig. 3 from 25° to 19° leads to an approximation to the value  $\text{H}_2\text{F}_4$  as the molecular weight of hydrogen fluoride at the point of liquefaction. Now, bearing in mind the analogies between water and hydrogen fluoride already noticed, it is worth pointing out that this determination of the weight of the physical molecule of hydrogen

fluoride agrees with Raoult's estimation of the probable value of the physical molecule of liquid water obtained by experiments on the influence of soluble substances in lowering its melting point (*Ann. Chem. Phys.* [6], 292).

Possibly a direct determination of the molecular weight of liquid hydrogen fluoride might be made on the principle of Raoult's method if an appropriate solvent could be found, together with a form of apparatus in which the use of glass was obviated. At present, however, we have no hope of being able to make such determinations.

XXV.—*Decomposition of Potassic Chlorate by Heat in the presence of Manganic Peroxide.*

By HERBERT MCLEOD, F.R.S.

THE familiar process of preparing oxygen by heating a mixture of potassic chlorate and manganic peroxide, first described by Döbereiner in 1832 (*Annalen*, **1**, 236—237), has been investigated by many chemists in the endeavour to trace the cause of the very ready decomposition of the chlorate; the matter, however, seems to be still rather obscure, and the experiments described in this note were undertaken in the hope of farther elucidating the subject.

Many years ago it struck me that the physical condition of the manganic peroxide was changed by heating with the chlorate, and I made a few experiments on the subject, but without any satisfactory result.

During the last three months a series of experiments has been made with various kinds of peroxide of manganese, and there is no doubt about the change of the peroxide.

The temperature employed has usually been that of boiling mercury, and the experiments have been carried out in the simplest way. A test-tube was weighed and about a gram of powdered potassic chlorate (which had been once recrystallised from water, powdered, and dried in a water-oven) and about 1/10th of its weight of manganic peroxide were introduced. The test-tube, attached by a bent tube and corks to a U-tube containing a solution of potassic iodide, was then placed into a wider test-tube, containing a small quantity of mercury, and the latter heated until the vapour of the mercury rose some distance above the mixture in the interior tube.

Potassic chlorate undergoes no perceptible decomposition at the temperature of boiling mercury; the powder, however, cakes together, and when the experiment is observed under the microscope there is an appearance of incipient fusion. In one experiment (I) (see Table, p. 193) 1·7107 grams of potassic chlorate was heated in mercury vapour for an hour and lost 0·0018 gram, or 0·105 per cent. In another case (XVII), 1·4402 gram of the chlorate was heated for 10 hours and the loss was 0·0024, or 0·167 per cent. This experiment was done under the microscope, and there were signs of fusion in 15 minutes after the heating commenced. The loss in weight was probably due to the presence of a small quantity of water.

The oxide of manganese used was obtained from various sources. Some, called "crystalline," obtained from Messrs. Hopkin and Williams, was in fragments of a crystalline structure; this was broken up in a mortar and levigated, the very fine particles being rejected. The rest was dried and sifted, the portion which remained between sieves with apertures of 0·19 and 0·16 mm. was kept and called "granular oxide;" it contains a small quantity of iron.

Some manganic peroxide was prepared by adding a solution of bleaching powder to a solution of manganous chloride, the precipitate was collected and washed, and afterwards boiled in acetic acid to remove any calcic carbonate present. It was then washed, dried, and heated for some time in a test-tube surrounded with mercury vapour. The compound was found from its loss on ignition to be  $Mn_2O_3$ .

A specimen of crystalline pyrolusite was used in some experiments. This was powdered and levigated, and the coarser portions employed.

I am indebted to Mr. V. H. Veley for two specimens of manganic peroxide, one of which was precipitated by the action of chlorine on pure manganous acetate (Trans., 1880, **37**, 581). Mr. Veley attributes to this compound the formula  $Mn_6O_{11} + xOH_2$ . When dried, first in the water-oven and afterwards in the vapour of boiling mercury, it lost 7·182 per cent. The other specimen was a piece of finely crystallised pyrolusite from Windsor, Nova Scotia; it contains a trace of iron.

The first experiment (II) was made with 1·0276 grams of potassic chlorate mixed with 0·1015 gram of "granular peroxide." The test-tube was heated in a beaker of mercury. At 13° below the temperature at which the mercury boiled, gas came off slowly, but at the boiling point the evolution was rapid. The solution of potassic iodide was coloured, and on titration with sodic thiosulphate it was found that the amount of chlorine which had been evolved was 0·0375 per cent. of the quantity of chlorate employed. The loss of weight of the test-tube and contents was 0·3975 gram, or 38·682 per cent. of the chlorate used. Taking 39, 35·37 and 15·96 as the atomic

weights of potassium, chlorine, and oxygen respectively, the percentage of oxygen in potassic chlorate is 39.166. The residue in the test-tube was extracted with water and filtered through a weighed filter, the manganic peroxide was now in a very fine state of division and weighed 0.1007 gram, or 99.211 per cent. of the quantity taken.

In the next experiment (III), the mixture was heated in the vapour of mercury; the mixture suddenly softened and swelled up, and gas was evolved so rapidly that some of the potassic iodide solution was projected from the U-tube, and white fumes were seen. Doubtless some of the mixture was carried over mechanically. The loss of weight was 39.145 per cent., the quantity of chlorine 0.0283 per cent., and the manganic peroxide recovered 98.5 per cent.

When the mixture of potassic chlorate and granular peroxide was heated by a gas flame, the evolution of oxygen was more violent, and some of the mixture was carried over by the gas. In one experiment (V), the loss was 39.380 per cent., and the peroxide recovered was only 97.294 per cent. In this case more chlorine was evolved, being 0.047 per cent. of the chlorate taken.

With the specimens of pyrolusite, the action was not so rapid, and less chlorine was evolved (VI, VII, and VIII).

With precipitated peroxide, the action is much more violent, the action being completed in about five minutes. There was usually a loss of solid matter from the tube, and more chlorine was evolved (IX, X, and XI).

It has been stated that the manganic peroxide loses its power of decomposing potassic chlorate, and therefore cannot be used over and over again (E. O. Brown, quoted by Baudrimont,\* *J. Chem. Soc.*, 1871, 24, 1151). To test this, a quantity of granular peroxide rather finer than that used in the previous experiments was heated in a test-tube with potassic chlorate over a gas flame, the mass washed with water, and the insoluble residue dried. This operation was repeated nine times, and the washed and dried oxide was heated with potassic chlorate in the vapour of mercury. In this case (XII), the quantity of peroxide was only 6.8 per cent. of the amount of chlorate, and yet the action was

\* This paper appeared in the *Journal de Pharmacie et de Chimie* [4], 14, 81—94, 161—177. (In the *Journal of the Chemical Society* it is quoted from *J. pr. Chem.*, which is obviously an error.) In the original, it is not stated that Brown had asserted that the oxide was exhausted by use, and in the same vol. of the *Journ. Pharm.*, p. 22, there is a report on the preparation of oxygen by Coulier, Limousin, J. Regnault, Jungfleisch, and Baudrimont, in which it is stated on p. 77 that the oxide does not lose its activity by previous use. I did not see these papers until the work was nearly completed; I would strongly recommend them to the attention of all chemists working on this subject.

very violent, and complete in two minutes. The loss was 39.121 per cent. and the amount of chlorine 0.045 per cent. The peroxide was entirely changed in appearance, and was brown instead of black. This shows that the peroxide cannot be exhausted by use, and the change of character seems to indicate that the peroxide had entered into chemical action and had been reproduced.

It will be noticed that in all these experiments an appreciable quantity of chlorine is evolved together with the oxygen. This evolution of chlorine is well known and has been frequently described. The questions arise, what is the source of this chlorine? and is its evolution a necessary accompaniment of the action of the manganic peroxide on the potassic chlorate?

The specimen of precipitated manganic peroxide which gave the largest quantity of chlorine was prepared from manganous chloride by the action of solution of bleaching powder, and when it was first prepared it contained a small quantity of chlorine. After having been heated in the vapour of mercury, however, this chlorine was eliminated. If all the chlorine evolved in Experiment IX had come from the manganic peroxide, the latter would have contained nearly  $2\frac{1}{2}$  per cent. of it.

When sodic chloride is heated in a test-tube with manganic peroxide over a gas flame, a very perceptible quantity of chlorine is evolved. A small quantity is also liberated when the mixture is heated to the boiling point of mercury, so perhaps it is more a matter of surprise that so little chlorine is present in the oxygen obtained from potassic chlorate and peroxide of manganese than that any should be produced.

To see if the addition of a body that would prevent the evolution of chlorine would affect the liberation of the oxygen, two experiments were made, in one of which (XIII) about half a per cent. of sodic carbonate was added to the mixture. At the boiling point of mercury, less than 6 per cent. of oxygen was evolved in half an hour. On heating over a gas flame, the action was not rapid and the fused mass appeared greenish; and on cooling, a small quantity of permanganate was observed. In the other experiment (XIV), about the same quantity of potassic carbonate was used; about 8 per cent. of oxygen was evolved at the boiling point of mercury, and more than the theoretical loss was observed after heating with a gas flame; this was probably due to loss when the test-tube melted.

As a considerable quantity of the manganic peroxide did not seem to be broken up when heated with the chlorate, some experiments were made to see if a much smaller quantity of the peroxide was capable of effecting the complete decomposition of the salt. In

Experiment XV less than 1 per cent. of the peroxide was used, and although the gas was evolved very slowly (the heating being continued for 5 hours and 20 minutes), yet ultimately almost the theoretical quantity of oxygen was liberated.

A still smaller quantity of peroxide also affects the chlorate, but much more slowly; in Experiment XVI only 0.1 per cent. was used, and after 22 hours 40 minutes 6.289 per cent. of oxygen had been evolved. An accident prevented the experiment being carried farther.

In those experiments in which the quantity of peroxide is very small, the white chlorate covers the granules and only a few black specks are visible. When such a mixture is heated, it is very curious to observe the formation and growth of grey spots starting from the granules, these spots increasing until the whole mass is uniformly grey. It seemed to be interesting to study the course of this change, and for this purpose a small quantity of potassic chlorate was placed in a test-tube with a single granule of the peroxide. The test-tube was inserted in a wider tube with some asbestos at the bottom, and the bulb of a thermometer was placed close to the bottom of the inner test-tube. A microscope with a 4-inch objective was arranged horizontally so that the granule of peroxide could be watched, the light from a gas flame being condensed on the object by a lens. The bottom of the outer tube was heated by a gas flame; and when the temperature reached 350° or thereabouts there were signs of fusion around the granule of peroxide, and the black mass appeared to glisten as if wetted or attacked; as it was not possible to maintain the temperature very constant, it was allowed to rise until the chlorate was all fused, when the peroxide was found to be broken up into minute fragments, each of which was a nucleus from which gas bubbles rose. On cooling, the fused mass had a distinct pink tinge as if permanganate had been formed; the colour could not have been due to potassic ferrate, for the tint produced by this compound is quite different.

In another experiment (XVII), to which reference has previously been made, 1.4402 grams of chlorate were heated for 10 hours in the vapour of mercury before the microscope; the loss was only 0.167 per cent. A fragment of granular peroxide weighing 0.0002 gram or 0.014 per cent. was then introduced and the heating recommenced. Minute particles soon became detached from the fragment, and the chlorate fused and flowed down in a stream between the glass and the rest of the salt, carrying the particles with it. The tube was allowed to cool and examined, and the mass was found to present the appearance so often observed; the grey stain having spread for some distance from the granule. The heating was continued for 4½ hours,



and some of the chlorate fused. The loss was 0·847 per cent. On cooling the mass was pink.

In Experiment XVIII, a brilliant crystal of pyrolusite from Windsor, Nova Scotia, was placed in a test-tube containing powdered potassic chlorate. This was heated in the vapour of mercury before the microscope. The salt soon fused in contact with the crystal, and an action was seen to take place on the surface of the latter. The crystal afterwards broke up into fine needle-shaped fragments, and in 55 minutes the whole of the salt was fused. After cooling, the mass was pink.

The evolution of chlorine during the action of manganic peroxide on potassic chlorate, and also the pink colour which is seen when the manganese compound is used in small quantities, seem to indicate that the formation of a permanganate may have something to do with the rapid evolution of oxygen; this has often been suspected by chemists. Some experiments were instituted to endeavour to prove this presumption.

An experiment (XIX) was made to determine the temperature at which the potassic permanganate is decomposed. Some crystals of air-dried permanganate were powdered and heated in mercury. Gas began to come off at 250°, and the evolution was rapid at 260°; at 275° the decomposition ceased. The mass in the test-tube had not fused, but it was almost black, and when water was added a deep-green solution was produced. The loss on heating was 11·176 per cent. In two other experiments the loss was 12·14 and 12·136 per cent. respectively.

It is usually stated in text-books that potassic permanganate is decomposed by heat into potassic manganate, manganic peroxide, and oxygen, thus:— $\text{K}_2\text{Mn}_2\text{O}_8 = \text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2$ . Taking the atomic weight of manganese at 55, this would involve a loss of 10·126 per cent. of oxygen. The loss of 11·176 per cent. more nearly agrees with the equation  $10\text{K}_2\text{Mn}_2\text{O}_8 = 10\text{K}_2\text{MnO}_4 + 2\text{Mn}_2\text{O}_3 + 11\text{O}_2$ . The quantity required by this change is 11·139 per cent. The loss 12·14 agrees nearly with the equation  $5\text{K}_2\text{Mn}_2\text{O}_8 = 5\text{K}_2\text{MnO}_4 + \text{Mn}_3\text{O}_4 + 6\text{O}_2$ , which requires 12·15 per cent. Too much reliance must not be placed on these results, as no endeavour was made to obtain pure permanganate; the specimen used was a well-crystallised sample of the commercial salt.

Several experiments were made to try the effect of the presence of different quantities of potassic permanganate on the decomposition of potassic chlorate in contact with manganic peroxide. In XX, XXI, XXII, and XXIII the percentage of permanganate to the chlorate was 0·151, 0·201, 0·449, and 0·491 respectively, and it will be seen that as the permanganate increased the quantity of chlorine evolved

diminished, none whatever being liberated in the last case. In the first, where the very small percentage of permanganate was used, the quantity of chlorine is notably less than in other cases where chlorate and the granular peroxide were heated together (II, III, IV, and V). The presence of the permanganate, however, very perceptibly diminished the rate of decomposition of the chlorate.

When the percentage of permanganate was raised to 2.3 (XXIV), the time was still further prolonged, so that in 1 hour 50 minutes little more than two-thirds of the chlorate was decomposed. The residue, after heating, contained manganate.

A mixture of nearly equal quantities of potassic chlorate and potassic permanganate was heated in mercury (XXV), the permanganate underwent its usual decomposition, there being 11.468 per cent. of its weight of gas evolved below  $275^{\circ}$ . On again heating in mercury, gas came off freely at  $350^{\circ}$ , and quickly at  $356^{\circ}$ . The mass was caked but not fused: on farther heating in the vapour of mercury for 35 minutes, very little more gas was evolved. Almost the whole of the oxygen of the chlorate was liberated. On adding water to the residue, the solution was green.

Another similar mixture (XXVI) was heated in mercury vapour. Gas at first came off rapidly and then diminished in quantity; it subsequently came off very rapidly, and some solid was carried over mechanically; the decomposition was completed in 10 minutes. The residue was not fused, and was found to contain manganate. The loss was 0.2425 gram, whereas the quantity of oxygen that might be expected from the permanganate and chlorate is 0.2404; the excess of loss was probably due to the solid that was carried over.

These experiments would seem to indicate that potassic manganate will not assist the decomposition of the chlorate, and that when the mixture of chlorate and permanganate is heated, the former is decomposed by the oxide of manganese liberated during the decomposition of the latter.

When potassic chlorate is fused with a very small quantity of manganic peroxide, a pink colour is observed in the mass on cooling, as before stated. When this pink mass is fused over a flame, oxygen is evolved, but the colour persists until nearly all the chlorate is decomposed; it then becomes greenish, and when further heated the fused residue of chloride has a brownish appearance. If the pink colour is due to permanganate, as seems most probable, it would appear to indicate that the permanganate is being continually reproduced as rapidly as it is decomposed by the heat, for the above Experiments XXI to XXVI prove that permanganate is decomposed in the presence of potassic chlorate. When the peroxide is used in large quantities, the pink colour is masked by the black oxide, although

it can hardly be doubted that it is really formed. This observation seems to supply the key to the question.

At first sight, it appears impossible that a compound can be formed at a temperature at which it is decomposed, but we have a somewhat analogous case with ammonia, which is decomposed by electric sparks, and yet when sparks are passed through a mixture of hydrogen and nitrogen, small quantities of ammonia are formed.

It has been stated by H. N. Warren (*Chem. News*, 58, 247) that when potassic chlorate and manganic peroxide are heated in an iron tube and the residue extracted with water, the solution is alkaline. I have often tested the solutions obtained from the residues after heating in test-tubes, but have never been able to recognise the faintest trace of alkalinity; the same result was found with the residue after heating in a platinum crucible; but if the residue had been strongly ignited, the solution was alkaline.

It has been shown by Eccles (*J. Chem. Soc.*, 29, 857) that potassic perchlorate is not formed when potassic chlorate and manganic peroxide are heated together; and I have found that when perchlorate is heated with the peroxide to the temperature of boiling mercury it does not lose oxygen. To the residue some potassic chlorate was added and the mixture again heated, when nearly the theoretical quantity of the oxygen from the chlorate alone was evolved. This observation entirely confirms that of Eccles.

If the manganic peroxide undergoes a chemical change, first entering into combination and then being reproduced, it seemed to be of interest to try the effect of one of the other oxides of manganese, for if this acted similarly it might be expected that after the action it would be found to have been changed into the peroxide.

Some precipitated manganic peroxide was heated in a platinum crucible to dull redness and weighed. It was then ignited for 45 minutes, by which it is said to be converted into  $Mn_2O_4$ . Some of it was mixed with potassic chlorate and heated in the vapour of mercury (XXVII). The mass fused and the chlorate was entirely decomposed although very slowly; very little chlorine was evolved. The insoluble residue was a little heavier than the oxide taken, amounting to 100.929 per cent.

Another quantity of the ignited oxide was heated in a muffle for two hours, when it lost 1.304 per cent. Some of this oxide was mixed with the chlorate and heated for three hours in the vapour of mercury (XXVIII). No chlorine was evolved, but the chlorate evolved nearly the whole of its oxygen. The oxide recovered was 98.071 per cent. of that used. If the oxide had been entirely transformed into  $MnO_2$  about 114 per cent. should have been collected. In a note to the Report of Messrs. Coulier, &c., above quoted, it is said, on p. 27, that

$\text{Mn}_3\text{O}_4$  is no less active than  $\text{MnO}_2$ . Baudrimont (*loc. cit.*, p. 163) states that  $\text{Mn}_3\text{O}_4$  acts more feebly than  $\text{MnO}_2$ .

It may be the fact that only a very small portion of the manganic peroxide is converted into another compound, the remaining portions merely acting as nuclei for the liberation of gas. It is noticeable that in the test-tubes in which the mixture of potassic chlorate and the peroxide is heated, a deposit of very fine powder is always observed on the glass which has been in contact with the mixture. This adheres firmly and is not removed by merely washing with water. Probably this represents some of the peroxide which has been reproduced.

Two experiments were made with a mixture of chlorate and platinum-black (XXIX and XXX), to see if a substance which might be expected to be chemically inert would assist in the decomposition of the chlorate, the particles acting merely as nuclei; in the first, 19.345 per cent. of gas was evolved in one hour, and in the other the mixture was heated for  $9\frac{1}{2}$  hours with two interruptions; when weighings were made, 28.111 per cent. of oxygen was evolved, so that the chlorate was far from being entirely decomposed. The most remarkable result was the evolution of about 0.02 per cent. of chlorine, so possibly a platinate or platinite was formed and immediately decomposed; the chlorine, however, may be due to insufficient washing of the platinum-black, which was made by reducing platinic chloride by sodic formate.

From the foregoing experiments, the mechanism of the action of manganic peroxide on the potassic chlorate, under the influence of heat, seems to be something of the following kind:—Firstly, the peroxide acts on the chlorate forming permanganate, chlorine, and oxygen.  $2\text{MnO}_2 + 2\text{KClO}_3 = \text{K}_2\text{Mn}_2\text{O}_8 + \text{Cl}_2 + \text{O}_2$ . Chlorine is certainly evolved as soon as the action commences. The permanganate then undergoes decomposition by the heat, producing manganate, an oxide of manganese and oxygen; for simplicity we may use the ordinary equation  $\text{K}_2\text{Mn}_2\text{O}_8 = \text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2$ . The third stage is not quite so clear; it is very improbable that the manganate is transformed into permanganate by the oxygen from the chlorate, for in Experiments XXIV and XXVI, in which permanganate and chlorate were heated together, manganate remained in the residue. It is more likely that the manganate is acted on by more chlorine produced by the action of the peroxide on fresh chlorate, thus,  $\text{K}_2\text{MnO}_4 + \text{Cl}_2 = 2\text{KCl} + \text{MnO}_2 + \text{O}_2$ . I have found that when chlorine is passed into the residue obtained by heating potassic permanganate, the residue being heated in the vapour of mercury, chlorine is absorbed and oxygen evolved. In this case, however, the action proceeds farther, for not only is the potassium transformed into chloride but much of the manganese is also converted into chloride.

	Potassic chlorate used.	Manganic peroxide used.		Other bodies used.		Loss.		Chlorine, per cent. on potassic chlorate.	Manganic peroxide recovered. Percent. on that used.	Source of heat.	Time of heating.	
		Grams.	Per cent. on chlorate.	Grams.	Per cent. on chlorate.	Grams.	Per cent. on chlorate.					
I.	grams. 1·7107	—	—	—	—	0·0018	0·105	—	—	mercury vapour	h. m. 1 0	Salt caked in test-tube.
II.	1·0276	granular 0·1015	9·877	—	—	0·3975	38·682	0·0375	99·211	mercury	—	Gas came off slowly 13° below boiling point of mercury. When mercury boiled, gas came off quickly.
III.	2·3714	granular 0·2467	10·403	—	—	0·9284	39·145	0·0283	98·500	mercury vapour	—	Gas came off rapidly, mass softened and swelled up; some of the potassic iodide projected from U-tube.
IV.	1·0977	granular 0·1107	10·085	—	—	0·4220	38·444	0·044	—	mercury vapour	0 30	Mass grey, and swelled up in 3 min. Gas came off regularly. Action complete in 15 min.
V.	1·0203	granular 0·1035	10·144	—	—	0·4018	39·380	0·047	97·294	gas flame	—	Gas came off quickly. Some white deposit found in delivery tube.
VI.	1·0041	crystalline 0·1013	10·088	—	—	0·3887	38·711	0·0045	96·742	mercury vapour	1 0	Gas came off rather slowly. Mass fused up.
VII.	1·0674	crystalline 0·1015	9·509	—	—	0·4138	38·767	0·0134	—	mercury vapour	—	

	Potassic chlorate used.	Manganic peroxide used.		Other bodies used.		Loss.		Chlorine, per cent. on potassic chlorate.	Manganic peroxide recovered. Per cent. on that used.	Source of heat.	Time of heating. h. m.	
		(grams.	Per cent. on chlorate.	Grams.	Per cent. on chlorate.	Grams.	Per cent. on chlorate.					
VIII.	1.0035 grams.	crystalline Nova Scotian 0.0993	9.895	—	—	0.3913	38.493	0.028	97.482	mercury vapour	1 45	Gas came off regularly. Almost stopped in 8 min. Plug of solid had been forced up tube. Mercury boiled more rapidly, and more gas came off.
IX.	1.0367	precipitated 0.1105 Voley's	10.659	—	—	0.4068	99.240	0.258	—	mercury vapour	0 10	Violent action which ceased in 5 min. Some $\text{MnO}_2$ carried over with the gas.
X.	0.9928	precipitated 0.0968	9.750	—	—	0.3922	39.504	0.115	—	mercury vapour	—	Gas came off violently, plug of solid blown up tube, and became incandescent. Finished in 4 min.
XI.	0.9874	Voley's precipitated 0.0922	9.338	—	—	0.3911	39.609	0.087	96.746	mercury	—	Bubbles passed during heating. At $320^\circ$ U-tube contained oxygen. Evolution violent at $340^\circ$ , and complete in 15 sec. Mercury boiled at $353^\circ$ . No more gas in 10 min.

XII.	0.8535	granular, which had been used 9 times 0.0584	6.842	—	0.3339	39.121	0.045	94.007	mercury vapour	0.20	Gas came off very quickly, finished in 2 min. White fumes in U-tube. $MnO_2$ very finely divided. Gas came off very slowly, but mass fused. Action not rapid. During fusion, the liquid appeared greenish. Small trace of permanganate when cold. $MnO_2$ not much broken up.
XIII.	1.1126	granular 0.1027	9.230	0.0065	0.584	5.779	0	—	mercury vapour	0.30	
					0.4329	38.908	0	100.081	gas flame	—	
XIV.	1.0013	granular 0.1038	10.366	0.0069	0.599	8.199	0	—	mercury vapour	0.30	Mass grey in 2 min. Swelled up in 4 min. Liquid in 6 min. Gas came off slowly. Action rapid. Part of mass became red hot. Test- tube was attacked. $MnO_2$ not much broken up. Black spots appeared in 5 min. The mass became grey all over and fused in 6 min., and effervesced; gas came off slowly. Grey spots grew in the chlorate. After 15 min. gas bubbles were formed, and the mass seemed semi- fused. In 40 min. the mixture was fused.
					0.4034	40.287	0	99.036	gas flame	—	
XV.	1.2438	granular 0.0116	0.932	—	0.4752	38.205	0.0069	81.896	mercury vapour	5.20	
XVI.	1.1131	granular 0.0011	0.099	—	0.0700	6.289	0	—	mercury vapour	22.40	







	Potassic chlorate used.	Manganic peroxide used.		Other bodies used.		Loss.		Chlorine, per cent. on potassic chlorate.	Manganic peroxide recovered. Per cent. on that used.	Insol. residue recovered. Per cent. on $Mn_2O_4$ used.	Source of heat.	Time of heating. h. m.	
		Grams.	Per cent. on chlorate.	Grams.	Per cent. on chlorate.	Grams.	Per cent. on chlorate.						
XXVI.	0.4867	—	—	potassic permanganate 0.4629	95.1100	2.125	—	0	—	—	mercury vapour	0 10	Gas came off at first rapidly, then slackened, then very rapidly. Some solid carried over. Mass not fused. Contained manganate.
XXVII.	1.0708	—	—	$Mn_2O_4$ 0.1076	10.0480	4.113	38.410	very little	—	100.920	mercury vapour	—	Gas came off very slowly. Mass fused.
XXVIII.	1.1438	—	—	$Mn_2O_4$ 0.1037	9.0700	4.361	38.111	0	—	98.071	mercury vapour	3 0	Mass blackened, fused, and effervesced.
XXIX.	1.2125	—	—	platinum black 0.1005	8.2890	2.346	19.345	0.023	—	—	mercury vapour	1 0	Mass blackened, fused, and effervesced.
XXX.	1.1892	—	—	platinum black 0.1148	9.6510	2.943	24.748	} .020	—	—	mercury vapour	3 15	
						0.3088	25.967		—	—	—	2 0	
						0.3343	28.111		—	—	—	4 15	

If this took place in the preparation of oxygen, the solution obtained by extracting the residue with water would contain manganese, which is not the case. Moreover, manganous chloride cannot exist at a high temperature in the presence of potassic chlorate, for it is immediately transformed into an oxide with evolution of chlorine. If the chlorine, which might be produced by the action of the peroxide directly on the chlorate, is thus absorbed by the manganate, it fully explains the very small quantity of chlorine that is evolved, for in the case in which the largest proportion was found (IX), when precipitated peroxide was used, it corresponds to only 6 per cent. of the peroxide present, and as the action in this case was of a very violent character it is not improbable that much of the chlorine was due to the subsequent action of the peroxide on the potassic chloride. In the experiment in which granular oxide was used and the mixture heated over a gas flame (V), the quantity of chlorine corresponds to little more than 1 per cent. of the peroxide.

The table (p. 191, *et seq.*) contains the details of the experiments referred to in the paper; they are not, however, given in the order in which they were actually made.

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## XXVI.—*Contributions to the Chemistry of Lignification. Constitution of the Jute Fibre-substance.*

By C. F. CROSS and E. J. BEVAN.

SINCE the publication of earlier papers on this subject (Trans., 1882, 90; 1883, 18) we have continued to prosecute our researches in various directions, certain of which have led to results from which more positive conclusions may be drawn as to the molecular constitution of this group of compound celluloses. Of these we proceed to give a short account. The investigations have been, for the most part, confined to the jute-fibre, than which we have found no better representative of the group of lignified celluloses. With regard to the term lignocellulose, we should, perhaps, explain at this point, that it recommends itself as being a sufficient description, without containing any suggestion as to the nature of the process by which they are formed, and which we do not think, speaking from the chemical point of view, is by any means completely elucidated.

Although from its nature the jute-fibre is an aggregate, it exhibits, notwithstanding, the constancy in composition and properties which

denote a chemical individual. The simplest expression of its elementary composition is the empirical formula  $C_{12}H_{18}O_9$  ( $C = 47.0$ ,  $H = 6.0$ ,  $O = 47.0$ ); whilst its proximate resolution into *cellulose* (78—80 per cent.) and *non-cellulose* (20—22 per cent.), may be represented by the formula  $3C_6H_{10}O_5, C_6H_6O_3$ . For the moment, we advance this as a statistical rather than a molecular expression, leaving it to the experimental evidence to be adduced to show in what degree it is established in the latter and more definite aspect. We shall show, in the first instance, that the more oxidisable constituents of the jute-fibre, to which is applied the neutral term non-cellulose, are compounds, or a compound characterised by an atomic ratio,\* approximating to  $C_6 : H_6 : O_3$ , and associated with the cellulose in chemical rather than mechanical union.

The intimate nature of this union is shown *first* in its resistance to the action of all simple hydrolytic agents. The alkalis in aqueous solution, the dilute mineral acids, such as have neither oxidising nor reducing properties, attack the fibre in proportion to temperature and duration of action. The result is a solution of the fibre substance, in quantity from 1 to 30 per cent. of its weight, according to the conditions, but without producing any essential chemical change in the insoluble residue (Trans., 1882, 100). In illustration of this point, we cite here the results of the "mercerising" treatment (*Watts's Dictionary*, New Edition, "Cellulose"), as applied to the jute-fibre.

Solution.	Temp.	Loss of weight.	Time.	Percentage cellulose† in product.		
1 per cent. NaOH ..	boiling	7 per cent.	10 mins.	79.1	77.8	78.7
33 " " ..	18°	7.9	1 hour	78.5	78.7	—
33 " " ..	18	9.6	48 hours	79.1	—	—
33 " " ..	18	14.3	7 days	78.9	—	—
33 " " ..	18	14.8	14 "	78.7	—	—
33 " " ..	80	13.2	1 hour	78.5	79.8	—
50 " KOH ..	18	14.2	7 days	79.9	—	—

The structural changes attending the action are profound, as they are in the case of cotton. The individual fibrils increase in thickness at the expense of length to the almost entire obliteration of the central canal; at the same time the union of the fibrils into bundles is more or less completely resolved, and the splitting up of the bundles is accompanied by the development of a wavy outline. So

\* The empirical formula actually deduced from the experimental results given in this paper is  $C_{76}H_{80}O_{37}$  (see pp. 207 and 213).

† The cellulose in these determinations serves as a constant to which to refer possible variations of the non-cellulose.

that, with the increased softness, the increased fibre has an external resemblance to wool. This increased softness is to be noted as a distinction from the pectic fibres or pecto-celluloses, which are hardened by such treatment. Reverting to the chemical features of these hydrolytic changes, the product does not differ in any essential point from the original fibre: the aggregate composition ( $C, H, O$ ), the proportion of cellulose to non-cellulose, and the characteristic properties of the latter persist unchanged.

The structural changes determined by the dilute acids, on the other hand, are opposite in character. The fibre substance surviving undissolved is converted into a hard friable modification, fracture taking place across the fibre bundles which are not resolved by the treatment. But the chemical feature of resistance of the combined molecule to hydrolytic resolution is equally characteristic in relation to this group of reagents.

The dissolution of the fibre substance in the ammonio-copper reagent, when carried out fractionally, also fails to *resolve* the compound molecule in question. In short, the fibre-substance is to be regarded as an aggregate, only in the sense that some portions (or molecules) are more susceptible of hydration than others, and although these may be attacked and dissolved wholly or in part by hydrolytic agents, they are not decomposed, but preserve intact their essential characteristics, which are those of the original fibre-substance.

The force of this conclusion is not diminished by the consideration of the resolutions effected by hydrolytic agents other than those above mentioned, or by these agents under extreme conditions of temperature. Thus, dilute nitric acid at  $60^{\circ}$ , sulphurous acid (7 per cent. solution) at  $90-100^{\circ}$ , and the aqueous alkalis at high temperatures, *resolve* it into cellulose and non-cellulose (soluble), at the same time attacking the cellulose more or less. But in these cases other conditions, whether of oxidation, reduction, or dehydration (condensation), are superadded, and our conclusion as to resistance of the lignocellulose molecule to simple hydrolysis, is unaffected by the results.

*Secondly.* In those reactions of the fibre substance which depend on its alcoholic characteristics (OH-groups), its molecular homogeneity is equally manifest. We give the statistics of the conversion of the lignocellulose into nitrates under varying conditions.

(a.) Nitrating acid: mixture of equal volumes of nitric acid (sp. gr. 1.43) and sulphuric acid (sp. gr. 1.8). Temp.  $18^{\circ}$ .

Duration of exposure.	Yield per 100 pts. fibre.
1 min.	125.2
2 mins.	129.2
3 „	140.0
4 „	149.0
15 „	146.0 secondary actions with con-
16 hours	131.0 version into soluble products.

(b.) Nitrating acids: I. As in (a). II. Nitric acid of 1.5 sp. gr., 1 vol.; sulphuric acid, sp. gr. 1.8, 1 vol. III. Nitric acid of 1.5 sp. gr., 1 vol.; fuming sulphuric acid, 0.75 vol.

In addition to the raw fibre (A), the modification resulting from the action of hot dilute hydrochloric acid (B) was included.

Duration of exposure in all cases 30 minutes at 18°.

Results: yield of nitrate per 100 parts dry fibre:—

	I.	II.	III.
A . . . . .	144.4	153.3	154.4
B . . . . .	143.8	152.8	152.7

A reaction according to the equation  $C_{12}H_{15}O_9 + 3HNO_3 = 3H_2O + C_{12}H_{15}O_6(NO_3)_3$ , is equivalent to a gain in weight of 44 per cent.: the conversion into the tetranitrate, 58 per cent. The formation of the latter appears, therefore, to be the limit of nitration of the jute-fibre; in other words, if we represent the lignocellulose molecule by a  $C_{12}$  formula, it will contain four alcoholic OH-groups, or two less than cellulose similarly represented.

To confirm the composition of these products and the equations above given, the specimen IIIA was analysed by Eder's method (*Ber.*, 13, 169), with the following result:—

0.453 gram gave 82.0 c.c. NO at 19° and 770 mm.; whence—

$$N \dots 10.5 \text{ per cent. } \text{Calc. } \begin{cases} C_{12}H_{15}O_6(NO_3)_3 & 9.5 \text{ p. c.} \\ C_{12}H_{14}O_5(NO_3)_4 & 11.5 \text{ „} \end{cases}$$

These nitrates resemble those of cellulose in all essential points. There is no evidence of any resolution of the molecule attending its combination with the acid radicle; the product is a nitrate of the lignocellulose, which again manifests itself as a chemical individual.

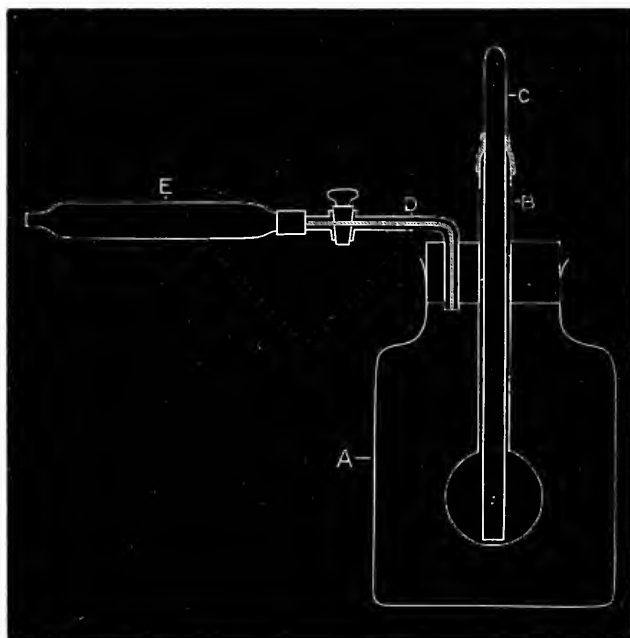
But, as we have previously pointed out (*loc. cit.*), the most characteristic reaction of the fibre substance is that with chlorine (in presence of moisture). The product of chlorination is not homogeneous, however, as are the nitrates: alcohol removes a chlorinated derivative of the non-cellulose, leaving, at the same time, after exhaustive treat-

ment, a certain proportion—about one-fourth—combined with the cellulose in such a way as to resist the action of solvents.

A statistical study of this reaction has enabled us to make some progress towards elucidating the problem of the constitution of the fibre substance.

*First*, with regard to the quantity of chlorine combining, 1·613 gram was chlorinated and dried in a vacuum over potassic hydrate (it was necessary to remove the hydrochloric acid in this way, as the chlorinated compound is appreciably soluble in water), and lastly, in the air-bath at 105°. We obtained 1·765 gram of dry chlorinated fibre; or 0·152 in excess of the original weight. The chlorine, estimated in the usual way, was found equal to 0·1511 gram; or 9·4 per cent., calculated on the original weight of fibre. This result was confirmed by other similar experiments. The numbers obtained we judged to be somewhat high, owing to the evidence of the presence of residual hydrochloric acid, in the chlorinated fibre blackening somewhat on heating. We therefore decided to measure the volume of chlorine disappearing in the reaction, and constructed an apparatus for the purpose already described in a note communicated to the *Chem. News*, 58, 215.

The essential portion of this apparatus is the reaction flask or bottle A. This is closed by a cork, through which pass two tubes.



The first, B, is blown out below to a thin bulb; it carries an outer tube of india-rubber above, through which is inserted a rod, C, of somewhat less diameter, and reaching nearly to the bottom of the bulb. The prepared fibre is introduced into the bulb, and at the required moment the bulb is shattered by a blow on C, and at once freely exposed to the chlorine atmosphere in A. A second tube, D, of narrow internal diameter, serves to connect the bottle with any convenient gas-measuring apparatus. The tube E contains a small quantity of the prepared fibre, and serves to indicate any diffusion of the chlorine outwards; which, however, we have never found to occur. It is as well to keep the gas atmosphere in A under a somewhat diminished pressure during the experiment; the absorption of the gas being followed (when an ordinary U-tube with mercury reservoir is used) by continual additions of mercury from the reservoir.

We need not enter in detail into the other precautions necessary to be observed, beyond remarking that the containing vessel was filled over warm water, and, on reinverting, a small quantity of water (5—10 c.c.) was allowed to remain in the bottom of the vessel, in order to provide for the complete absorption of the hydrochloric acid formed in the reaction.

We give the results of two, from amongst many concordant determinations.

(1.) 1.062, fibre; temp.  $18^{\circ}$ ; bar., 75S—18.

Duration in minutes....	10	15	30	40	45
Cl combining, c.c.....	52.5	53.5	59.0	60.0	60.0

Volume of Cl corrected to  $0^{\circ}$  and 760 mm.; 55 c.c. = 0.1764 gram.

At the conclusion of the experiment water was added to the containing vessel, the excess of chlorine expelled, and the hydrogen chloride formed was determined by titration, and found equivalent to 2.5 c.c. normal alkali; we have, therefore—

Cl in combination with fibre substance ..	0.0876
Cl as HCl formed in the reaction.....	0.0888
	<hr/>
	0.1764

The quantity of chlorine as hydrogen chloride in excess of the equivalent in combination is 0.0012.

The chlorinated fibre resulting from this experiment was boiled in solution of sodium sulphite, and the cellulose thus isolated, after washing and drying, was found equal to 0.846 gram, or 79.7 per cent. of the original.



(2.) 1.387 fibre; temp., 18.5; bar., 752 — 18.6.

Duration in minutes.    5 10 15 20 25 30 45 60 90 120 135 145 155  
Cl combining, c.c. . . . 47 53 57 59 62 63 69 72 75 78 80 82 82

Vol. of Cl corrected to 0° and 760 mm., 74.5 c.c. = 0.2390 gram.

Cl as HCl by titration. . . . . 0.1221 gram.

Whence Cl in combination . . . . . 0.1169    „

---

0.2390    „

The chlorine as hydrogen chloride in excess of the equivalent in combination is 0.0052 gram. Cellulose isolated 1.094 = 80.5 per cent. The percentage of chlorine combined with the fibre substance, and calculated on its original weight, is in (1) 8.2 per cent. in (2) 8.4 per cent.

*These results lead to the conclusion that the reaction is one of simple substitution of hydrogen by chlorine.\** We may extend this statistical inquiry by including what we had previously determined in regard to the composition of the chlorinated derivative. Our analytical results were as under:—

		Calculated for $C_{19}H_{18}Cl_4O_9$ .
C . . . . .	42.8	42.85
H . . . . .	3.4	3.38
Cl . . . . .	26.8	26.69

The fibre, on chlorination, we now find increases from 100 to 108.1, and from the above contains  $\frac{100 \times 8.1}{26.8}$ , that is, 30.2 of the chlorinated derivative of the non-cellulose. Subtracting this from the 108.1 we get 78, which agrees sufficiently well with the percentage of cellulose obtained. From this, we infer also that the chlorinated fibre contains no other compound, in addition to cellulose, but the chlorinated derivative of the above composition.

This is confirmed by the following experiments, in which the chlorinated derivative was investigated in fractions: 4.218 fibre chlorinated, washed, and exhausted with hot alcohol, the solvent always employed by us in isolating the chlorinated derivative for analysis. After exhaustion, the fibre weighed 3.635 = 86.2 per cent. of the original, still giving the brilliant colour reaction with sodium sulphite characteristic of the compound in question. Of this residual fibre, 1.232 grams was analysed for chlorine and found to contain 0.0225. This is equivalent to

\* We leave out of consideration, while admitting the possibility of combinations of chlorine without substitution as with CH—CH-groups.

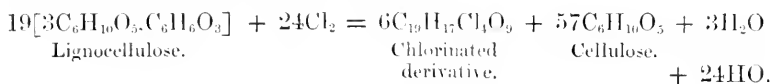
$0.0225 \times \frac{100}{26.8} = 0.084$  of the chlorinated compound, of which, therefore, continuing the assumption, the fibre contains 6.8 per cent. Subtracting this from 86.2, the percentage of fibre remaining after the original exhaustion, leaves 79.4 for cellulose. This agreement with the percentage estimated confirms the assumption, and supports the conclusion previously drawn as to the composition of the chlorinated fibre.

We must now consider, by way of parenthesis, one or two points of subsidiary and general bearing on the main argument, and the observations upon which it is founded. First, with regard to the errors in the method of determining the amount of chlorine combining, by observing the decrease in volume. We need not enter into a minute discussion of all the probable errors, for the reason that the decrease in volume in c.c. is a large multiple ( $>7$ ) of the percentage on the fibre to be calculated therefrom, and therefore the only error of moment is that resulting from the absorption of chlorine by the moist fibre.

The quantity of water introduced by the fibre in experiments (1) and (2) was less than 1 gram in either case; the corresponding absorption (solution) of chlorine would be from 1 to 2 c.c. This absorption would affect the percentage of Cl. calculated in the fibre by an amount equal to 0.2—0.3. This error requires further to be distributed between the chlorine as hydrogen chloride, and that in combination with the fibre substance. The former being taken as the difference between the observed absorption, and the chlorine as hydrogen chloride determined independently by titration, it will be seen that the error falls entirely on the former quantity.

The determinations of hydrochloric acid are subject to an error arising from the solubility of the chlorinated derivative in water and to its possessing an acid reaction. Washing the chlorinated fibre with saturated salt solution, in which the derivative is only slightly soluble, enabled us to minimise this error, which by direct observation of the "acidity" of the derivative—using litmus as the indicator as in the above titrations—we found could not exceed 0.1 c.c. of normal alkali in the second of the experiments detailed above. One other point remains to be noticed, viz., the work done by the chlorine used up in excess of the equivalent of that combining with the fibre substance. We carefully determined the quantities of carbonic acid formed in chlorinating the fibre, and in three experiments in which 4.5 grams of fibre was employed the quantities determined were 0.0156, 0.0210 and 0.0213, that is, from 0.003 to 0.005 per gram of fibre. The excess of chlorine in question would thus appear to be accounted for in the occurrence of a certain slight destructive oxidation.

Applying the correction for the excess of the estimated chlorine reacting it reduces the percentage upon the fibre substance from 8.3 to 8.0. This we take to be the quantity actually combining. Taking the formula of the chlorinated derivative as determined by analysis at  $C_{19}H_{18}Cl_4O_9$ , or at what is perhaps more probable,  $C_{19}H_{17}Cl_4O_9$ , and the aggregate formula for the non-cellulose from which it is formed as  $n(C_6H_6O_3)$ , we find that the main reaction of chlorination can be approximately expressed by means of simple multiples of these molecules; as under—



The ratio  $19C_{21}H_{36}O_{18} : 24Cl_2 = 100 : 2 \times 7.4$ .

The equation leaves us with a plus of 18 atoms H on the right hand side.

We must, however, at this point anticipate the conclusions subsequently established with regard to the non-cellulose. That it is a substance of considerable molecular complexity is of course to be presumed. The lowest atomic ratio deducible from a study of its constituent molecular groups is  $C_{76}H_{80}O_{37}$ , and although for statistical purposes this ratio may be taken at  $C_6H_6O_3$ , it is necessary to substitute the former expression in endeavouring to convert statistical into molecular quantities. The  $19 \times C_6H_6O_3 = C_{114}H_{114}O_{37}$  must be corrected to  $C_{114}H_{120}O_{35}(= 1.5 \times C_{76}H_{80}O_{37})$ . Leaving the cellulose out of consideration—as a constant—the chlorination of the non-cellulose may be represented by the equation—



which equation leaves us with a plus of only 8H on the right hand side, a quantity inappreciable by experimental method, which therefore would only require the employment of high multiples for its elimination.

With regard to the molecular proportion of chlorine taken up in the subsidiary reactions, it is easy to see that it equals  $2Cl_2$ , that is, in terms of the quantities represented by the above equations.

In regard to the cellulose isolated from the chlorinated fibre, we find it somewhat different in composition from the normal  $C_6H_{10}O_5$ . Our previous analyses (Trans., 1882, 104) showed that it approximated in composition to  $3C_6H_{10}O_5.H_2O$ , and we ought, perhaps, to speak of it rather as a cellulose-hydrate, of which the cellulose of the lignocellulose is the "residue." For the present, however, we are concerned in establishing the broad outlines of the chemistry of the fibre substance, and we are content to leave our results in the simplest terms necessary to convey clearly our main conclusions.

We have now to resolve the non-cellulose molecule, which, up to the present, has been dealt with as a homogeneous aggregate.

Following the lines of our previous communications (*loc. cit.*), we assume, as our starting point, the probable connection of the chlorinated compound with the derivative obtained by the action of this halogen on pyrogallol. The original suggestion of this line of research, we would remind the Society, is due to Dr. Armstrong.

We had previously shown (*loc. cit.*) that there was evidence of the presence of *mairogallol* in the chlorinated fibre, its reactions with sodium sulphite and with ferric chloride being indistinguishable from those of the phenol-derivative. Similarly, also, the isolated chloro-derivative yields chloroquinones by sublimation. Mairogallol yields trichloropyrogallol on reduction with zinc and sulphuric acid (Webster, *Proc.*, 1887, p. 131; Hantzsch and Schniter, *Ber.*, **20**, 2033). The chlorinated fibre similarly treated yields to ether a substance giving the deep blue reaction with barium hydrate, characteristic of this derivative. It has, however, been found impossible to isolate either trichloropyrogallol or mairogallol from the chlorinated fibre.

Taking the qualitative and *à priori* evidence before us as a basis for the hypothesis of the formation of the former in the chlorination of jute, we will again have recourse to the statistical method of proof.

As mairogallol contains 50·5 per cent. of chlorine, and the derivative under discussion 26·7 per cent., we conclude, on our assumption, that the latter contains 52 per cent. of the former, associated with a chlorine-free compound or compounds, amounting, therefore, to 48 per cent. of its weight. Or, taking the formulæ for these compounds in such multiples respectively that the numbers for chlorine shall be equal, and subtracting, we arrive at the result as follows:—

$$\begin{array}{rcl}
 (a.) & 11\text{C}_{19}\text{H}_{17}\text{Cl}_4\text{O}_7 & = \text{C}_{209}\text{H}_{157}\text{Cl}_{44}\text{O}_{99} = 5841 \\
 (b.) & 4\text{C}_{18}\text{H}_7\text{Cl}_{11}\text{O}_{10} & = \text{C}_{72}\text{H}_{28}\text{Cl}_{44}\text{O}_{40} = 3094 \\
 (c.) & \text{By difference} \dots & \text{C}_{137}\text{H}_{159} \quad \text{O}_{59} \quad 2747
 \end{array}$$

The proportion of the difference—that is, the chlorine-free hypothetical molecule (*c*)—to the original 11 mols. of chlorinated derivative (*a*) is 48 : 100. We have now to confirm this deduction by the experimental diagnosis of the hypothetical molecule in question.

In our earlier work (*loc. cit.*) we had observed that the chlorinated derivative had a powerfully reducing action on cupric oxide in alkaline solution, and concluded that it was a compound of a chlorinated body with a non-chlorinated derivative of aldehydic nature. That it was a compound and not a mixture we showed by the invari-

able results of the analyses of the compound prepared from various sources and variously fractionated. The aldehydic constituent we subsequently found to be *furfural* (Trans., 1883, 20). To liberate this aldehyde, alkaline hydrolysis of the chlorinated derivative is necessary; on then acidifying and distilling it is obtained in quantity. Thus, from 2 grams of jute chlorinated and treated in this way, we obtained 250 c.c. of distillate, giving a deep rose-red reaction with aniline acetate. Jute-cellulose, treated similarly, gives no furfural. This aldehyde is, moreover, a characteristic product of hydrolysis (acid) of all the lignocelluloses. We made an estimate of the yield of furfural from the jute fibre-substance, when decomposed by boiling with strong acids, using the approximate method proposed by V. Meyer (*Ber.*, 11, 1870), and based upon the colour reaction with aniline acetate. The quantities estimated in two experiments were 10.0 and 11.2 per cent. respectively (*Jour. Soc. Chem. Ind.*, 4, 11; *Watts's Dictionary*, New Edition, "Cellulose"). On the other hand, the isolated celluloses from such substances as jute, pinewood, and other fully-elaborated lignified fibres or tissues, yield no furfural, or at the most traces of it, under severe treatment. We have now to compare the composition of furfural with that of the hypothetical chlorine-free constituent of the chlorinated derivative expressed by the statistical formula, viz.,  $C_{137}H_{159}O_{59}$ , as follows:—

	Furfural. $C_5H_4O_2$ .	Hypoth. body. $C_{137}H_{159}O_{59}$ .
C.....	62.5	59.8
H.....	4.1	5.8

It would appear, therefore, that the furfural is associated in the hypothetical molecule with a body containing a relatively high proportion of hydrogen. This body we have had no difficulty in showing to be an acetic residue.

The presence of methyl-groups is proved by the evolution of methyl chloride from the chlorinated derivative when heated. We also obtained this gas in large quantity from the similar derivative which we prepared from esparto and described in our first paper (Trans., 1882, 94).

The fibre, when boiled with chromic acid, yields acetic acid in small quantity, but the most effectual way of isolating the acid is by dissolving the fibre in concentrated sulphuric acid in the cold, diluting and distilling; from 4.5 grams thus dissolved, after the solution was diluted to 250 c.c. and distilled,\* we obtained a distillate of 160 c.c.,

\* We treated in this way the same weights of both cotton and jute cellulose. In neither case did we obtain any volatile acid. The source of the acetic acid in the above experiment is therefore in the non-cellulose constituents of the fibre.

containing 0.180 gram of acetic acid, together with furfural. The distillate was redistilled from chromic acid, the second distillate boiled with silver oxide, filtered, and evaporated to dryness. Silver acetate crystallised out, and the crystalline residue yielded, on ignition, 64.7 per cent. Ag (calc.  $C_2H_3O_2Ag$  64.6). Acetic acid was thus proved to be the only volatile acid formed.

Reverting to the statistical comparison of the hypothetical molecule with furfural with our determinations of the proportion of this aldehyde to the fibre substance, and assuming that the acetyl radicle is present in the form of acetaldehyde, we infer, from the carbon percentages, that these aldehydes are associated in the proportion by weight of six of the former to five of the latter.

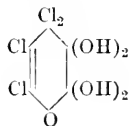
We may sum up our inferences as to the composition of the chlorinated derivative of the non-cellulose as follows:—

100 parts of fibre combine with 8 of chlorine; 108 of chlorinated fibre thus produced are made up of 78 of cellulose and 30 of chlorinated fibre. The 30 of chlorinated non-cellulose is made up approximately of 16 parts of mairogallol and 14 of the hypothetical molecule. 14 of the hypothetical molecule are made up of 7.6 parts of furfural and 6.4 of acetaldehyde.

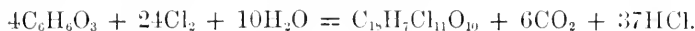
Having no further experimental evidence to adduce on the main subject of our inquiry, we would close our communication at this point, but we may, perhaps, be allowed to discuss certain of its general bearings.

With regard to the statistical method pursued, it is unnecessary to point out its imperfections. It must be judged by the exigencies of the case and by its results. We have made many ineffectual attempts to resolve the chlorinated derivative. We have closely studied mairogallol and the group of halogen-derivatives of the trihydric phenols, of which it is a member, with the view of finding a means of isolating it, or a product of its decomposition from the derivative. Our failure, it will be admitted, is in harmony with the conclusions drawn from the statistical investigation as to the nature of this complex molecule, that is the association of mairogallol—itself a very unstable molecule—in combination with such active molecules as furfural and acetic residues.

Hantzsch and Schniter regard mairogallol (*loc. cit.*) as a condensed derivative of a typical quinone-chloride molecule—



It is formed from pyrogallol by a destructive chlorination, which Stenhouse and Groves formulated as under:—



We made an approximate determination, by the absorption method described above, of the chlorine required to chlorinate pyrogallol in presence of cellulose. We dissolved 0.100 of the phenol in a little water, and added the solution to a pure cellulose fibre, which was then exposed to chlorine, as described. The absorption measured was 87 c.c. (at 18° and 756 mm.), from which, neglecting the  $\text{CO}_2$  formed, which we assume to be absorbed by the water present, we conclude that 0.25 of Cl was taken up; the quantity required by the equation being 0.33. We cite this in contrast to the chlorination of jute, which we have shown to be non-destructive, and in support of the conclusion that mairogallol being formed by the simple combination with chlorine, the non-cellulose of jute contains carbon-rings of similar arrangement to the typical molecule of mairogallol formulated above.

This inference, in conjunction with the ascertained furfural and acetyl groupings of the constituent atoms of the non cellulose, lands us in a region of possibilities, further entry into which would be on the basis of pure speculation. For the present it is sufficient to bear in mind that the conclusions we have arrived at generalise, and in no particular contravene what is known of this typical lignocellulose, the jute-fibre.

Having regard to the results obtained, we shall extend this statistical method of investigation to other members of the group of lignocelluloses. Of these there appear to be two main groups, (1), that of which jute is the type, and which, so far as we have been able to observe, is coextensive with lignification as defined by the physiologists, and as manifested in the earlier stages of growth; (2), the substances composing the fibre elements of perennial stems, that is, the woods proper. Of these, fir-wood (*Pinus abies*) may be taken as the type. Of the former, we have had occasion to investigate a considerable number, and have found the same chemical characteristics, not only in isolated bast-fibres of the same class physiologically as jute, for example, the bast of the various species of *Hibiscus*, of *Sida rhombifolia*, but also in fibres and fibro-vascular bundles of monocotyledons, for example, *Musa* and *Aloe* species, and even in the stony secretions of the pear, which, although of such widely different functions, is closely similar in properties to the jute-fibre substance.

Of results obtained with these various plant products we mention the following:—Chlorinated derivatives isolated from *Musa* (*Paradisica*) and Esparto, closely resembling the compound from jute

(Trans., *loc. cit.*). A quantitative investigation of the chlorination of *Sida* by the method described in this paper, giving 7.2 per cent. on the fibre of chlorine combining, with 7.9 per cent. chlorine as hydrogen chloride. The decomposition of the stony concretions of the pear by chlorination into cellulose and chlorinated non-cellulose, identical with that of jute, and by acid hydrolysis into furfural\* on the one hand (not glucose, as stated by Erdmann), and insoluble condensation-products on the other.

With regard to the actual processes of lignification, of which the chemical identity is established for so wide a range of plant elements, we would offer a few observations, based upon our investigations of jute.

We have recently had the opportunity of investigating the development of the fibre in the living plant. We find that from the earliest appearance of the fibre|bundles, for example, in sections cut a few centimetres below the growing point, they have all the chemical characteristics of the mature fibre. In the isolated fibre, we find no sensible variation in the proportion of cellulose to non-cellulose, nor in their mode of combination, throughout the entire length of 2 to 3 metres. This evidence appears to carry with it the suggestion that both cellulose and non-cellulose may have a common and simultaneous origin in a parent substance, and that lignification is the result of progressive modifications and differentiations of this original complex molecule.

On this view the chemistry of the second group of lignocelluloses, the woods, would be a continuation of this process of modification. We have reason to hold that, in the earlier stages of growth, they are similar in composition to the members of the first group. In their mature condition, on the other hand, we find them characterised by a higher carbon percentage, 49—51, as compared with 46—48, and a higher proportion of non-cellulose, 50—60, as against 20—30.

The physiologists are accustomed to speak of vegetable matter as "dead" when removed from the sphere of the vitally active cells. To the chemist no such sharp line of demarcation exists. The substances composing the tissues of plants, and notably the lignocelluloses, are, as is evident from their nature, capable of a long series of intrinsic modifications, and we think due weight should be given to such considerations in all endeavours to advance from our present very imperfect knowledge of the chemistry of elaboration.

In conclusion, we would briefly summarise the main points which we have thus endeavoured to establish, with regard to the constitution of the jute fibre-substance.

- (1.) A compound of cellulose and non-cellulose, empirically  $C_{12}H_{18}O_9$ ,

\* Or a carbohydrate yielding furfural.



of the general chemical features of the celluloses, resisting hydrolysis and yielding explosive nitrates, of which the highest is the tetra-nitrate.

(2.) The non-cellulose is a complex molecule, from the products of resolution of which, by chlorination and hydrolysis, we infer it to contain the following groups of molecules:—

(a.)  $C_{18}H_{18}O_{10}$ , ketone transitional to a quinone, chlorinated directly to form mairogallol: (b.)  $C_5H_4O_3$ , furfural in combination, by condensation with (a), and with (c) an acetic residue. These are combined in the approximate molecular proportion (a) 2, (b) 6, (c) 5,  $= C_{76}H_{80}O_{37}$ .

(3.) The lignocelluloses in the earlier stages of growth are constituted on this type. The true woods, on the other hand, appear to represent a more condensed type.

## XXVII.—*The Atomic Weight of Chromium.*

By S. G. RAWSON, B.Sc., Demonstrator of Chemistry, University College, Liverpool.

A GREAT many investigations have been made of the atomic weight of this element, and the result, leaving on one side the work of the earlier experimenters, seems to place the value between 52.0 and 52.5. In consequence of this considerable difference, it seemed to me that a redetermination of the atomic weight might be of service.

The first experiments of any value were those made by Péligot (*Compt. rend.*, 19, 609 and 734; 20, 1187; 21, 74), who analysed chromous acetate, and came to the conclusion that the atomic weight was about 52.5, the earlier results of Berzelius having given 56. Berlin, in an important paper (*J. pr. Chem.*, 37, 509, and 38, 149), obtained results from which he deduced an atomic weight of 52.51, if  $O = 16$ ; the method employed was to reduce silver chromate with alcohol and hydrochloric acid, and then having thoroughly washed the silver chloride formed, to heat this in the flask in which the reduction took place. The washings were then treated with ammonia, and the precipitated hydrate filtered, dried, and ignited. The objection to this plan is, as Siewert pointed out, that silver chloride is soluble in a chromium chloride solution, and consequently traces of silver chloride are estimated with the chromium hydrate; this error would tend to raise the atomic weight of the metal. Siewert's

(*Zeitschrift gesamm. Wissenschaften*, **17**, 530) own plan was to fuse the sublimed violet chloride of chromium with sodium carbonate and nitre, then to precipitate the chlorine with silver nitrate in the presence of nitric acid, and weigh the silver chloride thrown down. In some experiments on the silver dichromate, both the silver chloride and the chromium hydrate were weighed. The mean of all his results was that if  $O = 16$ ,  $Cr = 52.129$ .

Another series of experiments was carried out by Kessler (*Pogg. Ann.*, **95**, 208, and **113**, 137), who compared the oxidising power of potassium dichromate with that of potassium chlorate, the solutions used for titration being ferrous chloride and arsenious acid. He deduced the molecular weight of  $K_2Cr_2O_7$  as equal to 294.013, whence the atomic weight of chromium is 52.116.

Moberg (*J. pr. Chem.*, **43**, 114) ignited anhydrous chromium sulphate and ammoniacal chrome-alum and weighed the residual  $Cr_2O_3$ . There are, however, two objections to his method—first, that it is difficult to obtain the pure anhydrous salts, and then, as has been recently shown by Lupton, it seems to be exceedingly difficult to completely decompose the sulphates, no matter how high the temperature of ignition may be.

Banbigny (*Compt. rend.*, **98**, 146), however, who has lately published some researches on this point, found that if a perfectly pure sulphate be taken, prepared according to the method indicated by him, and ignited, the decomposition is complete, and he gives as the mean of the results which he considers most trustworthy, the figure 52.16 for the atomic weight of chromium. Clarke, in his work on the "Recalculation of the Atomic Weights," also gives the results obtained by various other experimenters.

Passing on to my own work, I may mention that the balance used was of the short-beamed type, and was by Sartorius of Göttingen. I determined its sensibility, and the ratio of the arms of the balance to one another was also obtained and allowance made for this; the correction necessary, however, being very slight. In weighing, the method of vibrations was always used, a zero reading being taken both before and after weighing in every case, and the value of a scale division for the particular load was determined by shifting the rider 0.6 milligram at a time.

The weights used were made by Oertling, and had been specially adjusted. Mr. Chaney was kind enough to standardise two of the 10-gram weights for me, and found that  $10^A = 10.000077$ ;  $10^B = 10.000087$ .

From these, the actual values of the remaining brass gilded weights were determined. No correction was made for the platinum weights.

The idea on which I proposed to myself to work was of a two-fold nature. In the first place by the ignition of ammonium dichromate, I hoped to measure the nitrogen evolved, and to weigh the chromium sesquioxide which remained after ignition, and then, in the second place, to reduce the dichromate with alcohol and hydrochloric acid to the chloride, and estimate the oxide produced by direct precipitation with ammonia. Hence the only salt which I should require was ammonium dichromate, and this, from the readiness with which it can be bought of very considerable purity, and from the ease with which it can be recrystallised, was very suitable for the purpose. It is, moreover, permanent in air, is not hygroscopic, and the atomic weights of its constituents are amongst the best determined of all the atomic weights of the different elements; for, amongst many others, Stas and Regnault have both determined the atomic weights of oxygen and nitrogen.

As it is clear that the purity of the ammonium dichromate was of paramount importance, I endeavoured to secure this in the following way:—

#### *Purification of Ammonium Dichromate.*

8 ozs. of the purest ammonium dichromate which I could obtain was very carefully analysed and with practically negative results, so far as impurities were concerned. It was then recrystallised from water which had been thrice distilled, the weight of the crystals obtained being 5 ozs. The crystals were again dissolved, and the solution evaporated down on a water-bath with constant stirring until about 3 ozs. of the crystals in a mealy condition were obtained. These were again recrystallised and the crystals drained on a filter-pump, washed with cold water, and again dried by the filter-pump. This operation was repeated, and the crystals once more dissolved in water, and then as a trace of a basic salt might have been formed by the previous crystallisations, though the solution on inspection appeared absolutely clear and bright, it was filtered through a filter-paper, previously boiled and washed in pure water, and evaporated nearly to dryness on a water-bath with constant stirring. The mass was then again drained on the filter-pump, crushed, and dried in an air-bath at 100° for 36 hours, with occasional stirring, and finally placed in a desiccator for about a fortnight. In this manner it is hoped that the salt was obtained in a state of purity.

#### *Method A. Ignition of Ammonium Dichromate.*

A weighed amount of the dichromate was placed in a small, thin tube, which was then sealed up, and this was inclosed in a piece of

wide glass tubing, sealed at one end and drawn out and bent at right angles at the other, and loosely plugged towards this end with cotton-wool. The inner tube was then broken by a slight jerk, and the dichromate distributed along about one-sixth of the length of the outer tube; the latter was then connected with a series of U-tubes filled with calcium chloride, which in their turn were connected with a Sprengel pump. The apparatus was then exhausted and the tube cautiously heated in order that the evolution of nitrogen might be more under control. In spite of the greatest care, however, the dichromate burned, when once started, like so much tinder, and, in consequence, the nitrogen came off with such rapidity that I was unable to prevent some particles of chromium oxide from being carried away. Not only so, but it seems to me more than likely that traces of the dichromate itself might also be mechanically removed, and, perhaps, a minute quantity might even escape decomposition altogether, mixed as it is with the extremely voluminous and light residue of the oxide. I tried plugging the tube with asbestos and mixing the dichromate with a known weight of pure sand, but the results were not satisfactory. Besides these errors arising from imperfect mechanical appliances, and which might, no doubt, be overcome, there is a far more serious one in that the gas which is evolved is not pure nitrogen as it is usually stated to be. If the gas, as it is given off, be dried and collected in a suitable vessel over mercury, it will be seen to be of a very faint brownish colour with a nitrous smell and acid reaction. If the gas be shaken up with water the solution gives clearly enough with ferrous sulphate and sulphuric acid the ordinary reaction for nitric acid; and if the gas is allowed to remain standing over the mercury, the surface of this becomes coated with a slight white deposit, probably the nitrate. I also observed another curious fact in some rough experiments in which no drying took place and the tube was not plugged. The gas was passed through a series of empty bottles to serve as catch vessels for the oxide; in the first of these there was a strong smell of ammonia, and the gas had an alkaline reaction, whilst in the glass collecting-tube nitrous fumes were present, as mentioned above. I tried two or three different samples of dichromate with exactly the same results. In this connection, the appearance of the oxide is interesting, for instead of being of a bright green colour, as one would expect, I always found it to be mixed with numerous particles of a greyish colour, in fact, I should feel disposed to say that the whole was rather grey than green. These particles, when rubbed on paper, gave an olive-green streak, but if they were again ignited in the presence of air, then they assumed the ordinary green colour of oxide of chromium, and their streak was also of the usual tinge. It would seem that,

besides the primary reaction in which nitrogen and chromium oxide are mainly formed, there is a secondary reaction resulting in the formation of one or more of the oxides of nitrogen, and of an oxide of chromium of a composition not expressed by the formula  $\text{Cr}_2\text{O}_3$ . I give the result of an actual experiment.

Weight of dichromate taken = 1.29495 gram.

Volume of nitrogen at  $0^\circ \text{C}$ . and 760 mm. pressure, 111.946 c.c.

Volume of nitrogen calculated at  $0^\circ \text{C}$ . and 760 mm. pressure (if  $\text{Cr} = 52$ ), 114.740 c.c.

Volume of nitrogen calculated at  $0^\circ \text{C}$ . and 760 mm. pressure (if  $\text{Cr} = 52.5$ ) 114.292 c.c.

I assumed that the atomic weight of  $\text{O} = 15.96$ , of  $\text{N} = 14.02$ , and that at standard temperature and pressure a litre of nitrogen weighs 1.25700 grams.

*Method B. Reduction of Ammonium Dichromate to Chromium Chloride.*

In this series of experiments, as previously mentioned, a known weight of the dichromate was reduced with great care to chromium chloride, precipitated with the least possible amount of ammonia, and then ignited and the oxide weighed. It is clear, therefore, that besides ammonium dichromate four other compounds, namely, water, hydrochloric acid, alcohol, and ammonia, took part in the reaction. These substances all readily lend themselves to purification, and the method employed for this purpose in each case I will briefly indicate. A platinum dish of 200 c.c. capacity was taken and tared against another dish of the same size and almost the same weight, the difference in the weight between the two dishes being made up by means of a small piece of platinum foil. These two dishes were treated in all respects alike, when one was placed on the water-bath, so also was the other, and for the same time; they were ignited in a similar manner, and they were placed in desiccators for the same length of time, &c. In this manner the various corrections, at best uncertain, which would have been necessary in computing the actual weight of the dish, were obviated. They were both covered with platinum foil, but their covers were not weighed with them.

The dishes having been carefully tared, a known volume, viz., 100 c.c. of pure trebly distilled water was then evaporated to dryness, the dishes ignited, and again weighed. I was unable to detect any difference in their weight, and the experiment having been repeated once or twice with the same result, it was assumed that the water was pure. The hydrochloric acid was bought as the purest, but it was again distilled most carefully, and 100 c.c. evaporated as before, there being in this case also either no residue or one which was absolutely

inappreciable. With the ammonia, which was also redistilled, there was no residue, though in this case I only evaporated a much smaller quantity, namely 20 c.c. The alcohol, however, gave me at first a residue of 0.063 gram per 20 c.c. of alcohol taken, but after being again very carefully distilled, was found to be pure.

Having thus purified the materials and determined the errors, if any, introduced into the estimation by the reagents employed, it was now possible to make some determinations of the required atomic weight. As the same plan was adopted throughout, a short description of one experiment will suffice for all the others.

The two platinum dishes having been carefully cleaned were ignited, cooled in desiccators, and weighed against one another, the piece of platinum foil being adjusted until the difference between the two was reduced to an amount less than 1 mgrm., the exact difference being carefully noted. The finely ground ammonium dichromate was then placed in one dish, weighed, and the temperature and pressure noted; 10 c.c. of water were then added, and when the salt had dissolved, 10 c.c. of hydrochloric acid; then with great care, and in small quantities at a time, 10 c.c. alcohol were added, and the whole evaporated to complete dryness on the water-bath, the platinum dish serving as tare being also placed on the water-bath. The above treatment was again repeated, so that there should be no doubt as to the complete reduction of the salt. The residue was taken up with 10 c.c. of water, and then 2 c.c. of the pure ammonia solution were added, and the whole stirred with a platinum wire bent once at right angles. Another 10 c.c. of water were added, and 3 c.c. of ammonia, and the mass again thoroughly stirred with the wire, which was washed with 10 c.c. of water. The mass was then evaporated to complete dryness, placed in an air-bath, and heated at about 140° for five hours. The two dishes, with their loosely-fitting platinum lids, were next placed in a gas-muffle, the floor of which was covered with asbestos card, the dishes themselves resting on pipe-clay triangles. The temperature was slowly raised to redness, and maintained at that point for an hour; the evolution of ammonium chloride was perfectly under control, and I do not believe that a trace of the oxide was mechanically carried away. In the volatilisation of the ammonium chloride, it was, however, possible that a certain amount of decomposition might have taken place, and that a trace of chromium chloride might have been re-formed, for it was found that, if a mixture of the hydrate and ammonium chloride were heated in a long glass tube, closed at one end and contracted at the other, a considerable amount of the chloride was produced. It is true that the conditions obtaining in the two cases were very different, still as there was the chance that an error might be introduced, it was

necessary to provide against it. The ignited residue was, therefore, treated with water, and then a little ammonia added, and the whole again evaporated to dryness and ignited. The dishes were then removed from the muffle by means of a fork with two prongs made of brass wire and coated with platinum foil, and placed at once in desiccators, allowed to cool in the balance-room, and weighed, the temperature and pressure being noted. They were again heated for half an hour and weighed, and also a third time; if the last two weighings agreed, the result was accepted. In this way, throughout the whole process, there was no transference at any time of any of the material from one dish to another, no filtering, no handling of any of the apparatus employed, and no burning of filter-papers, the whole operation being of the simplest kind. The chromium oxide was always of a beautiful green colour, and its purity was tested by treating it with water and filtering. The filtrate was clear and colourless, and on evaporation gave no residue. There were in all eight estimations made, but the first one was spoiled by using too much ammonia for the precipitation, and the second through incompletely drying the residue in the air-oven before igniting in the muffle. The remaining six observations gave the subjoined results.

The assumptions made in the calculations were these:—

	grams.
1 litre of air at 0° C. and 760 mm. pressure weighs	1.293
Correction for 1 gram $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ at standard atmosphere .....	0.000446
Correction for 1 gram $\text{Cr}_2\text{O}_3$ at standard atmosphere .....	0.0001
Atomic weight of O .....	=15.96
Atomic weight of N .....	=14.02
Atomic weight of H .....	= 1.00

I give the experimental results and the value for the atomic weight of chromium deduced from each of them.

Weight of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ (corrected).	Weight of $\text{Cr}_2\text{O}_3$ (corrected).	Ratio of Cr : H.
1.01275	0.61134	52.130
1.08181	0.65266	52.010
1.29430	0.78090	52.020
1.13966	0.68799	52.129
0.98778	0.59595	52.016
1.14319	0.68987	52.059
	General mean .....	52.061
	Maximum difference.	0.120

From this it will be seen that my experiments give results corresponding to the lower limit for the atomic weight of this element, and further, make the value approximate very closely to a whole number. I do not know of any constant source of error in my experiments. The only point in which there might be, perhaps, a risk of loss, is in the ignition of the mixture of chromium hydrate and ammonium chloride, with the loss of a little of the chromium oxide as the ammonium chloride volatilises.

I have never had, however, any ground whatever for supposing that such was the case, and further, the platinum covers loosely fitted to the dishes would, I think, practically remove even the chance of any such source of loss. The appearance of the residue, also, did not lend itself to any supposition of this kind.

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XXVIII.—*The Decomposition of Carbon Disulphide by Shock.*  
(A Lecture Experiment.)

By T. E. THORPE, F.R.S.

It is usually stated in the text-books that only one compound of carbon and sulphur is known, viz., carbon disulphide, but the investigations of Hermann, Guignet, Löw, Sidot, and Raab have rendered it certain that several sulphides of carbon exist. The accounts which have been given of the nature and composition of these substances are, however, somewhat conflicting, and this fact induced me, some little time since, to begin some experiments with a view of obtaining further evidence on the subject.

Löw obtained a sesquisulphide,  $C_2S_3$ , by the action of sodium-amalgam on carbon disulphide, and Raab prepared a compound,  $C_5S_2$ , which he termed *pentacarbon sulphide*, by the action of sodium alone on the disulphide. One difficulty attending the use of the amalgam consists in the necessity of removing the mercury, and this, in Löw's process, involves the employment of sulphuretted hydrogen; in the other method the sodium becomes gradually coated with a thin crust of the product, and the action ceases after a time. It occurred to me that possibly better results might be obtained by the use of the *fluid alloy* of potassium and sodium, which is very mobile, and which, it was hoped, could be readily detached from the incrusting mass by shaking, and thus cause fresh surfaces of the mixed metals to be exposed to the action of the disulphide. Accordingly, as a prelimi-



nary experiment, I treated a small quantity of rectified carbon disulphide, dehydrated by phosphorus pentoxide, with a few grams of the fluid alloy made by squeezing the two metals together through a sodium-press. After standing for a few hours, considerable quantities of a yellowish-brown powder were seen to have incrustated the globules of the alkaline alloy; but on shaking the bottle to detach the crust, the contents exploded with a loud report, and my hand was coated with a black deposit apparently consisting of finely divided carbon.

Further experiments on the yellowish-brown powder showed, in fact, that it is highly explosive; on simply pressing a few particles of it with a glass rod, it detonates with even more violence than diamine diiodide (iodide of nitrogen).

On reflecting on the circumstances of the explosion, it seemed to me that the deposit of carbon on my hand was far larger than could possibly have come from the decomposition of the yellowish-brown powder itself. The only other substance present which could have furnished such a deposit was, of course, the carbon disulphide. Now, carbon disulphide is an endothermic compound: when formed from its elements, and as liquid, it absorbs, according to Thomsen, 19,610 calories. Hence it was not improbable that it would be found to behave like acetylene, cyanogen, nitric and nitrous oxides, the oxides of chlorine, &c., and experience decomposition by sudden and violent shock. On this supposition, the carbon disulphide had in all probability been resolved into its elements by the violent explosion of the relatively small quantity of the yellowish-brown powder, just as Berthelot has shown that acetylene and cyanogen may be so resolved by the explosion of mercuric fulminate. A very few trials proved that this was actually the case, and as the experiment forms an exceedingly easy and perfectly safe method of demonstrating the resolution of an endothermic compound by shock, as a class illustration, I venture to bring it under the notice of the Society.

The apparatus required consists simply of a thick glass tube about 600 mm. long and 15 mm. wide, fitted at one end with a caoutchouc cork through which pass two stout wires or thin rods. On the end of one wire is fixed a small brass or iron cup like that of an ordinary deflagrating spoon, and the other is so bent as to nearly touch (to within 2 or 3 mm.) the bottom of the cup in which is placed about 0.05 gram of mercuric fulminate. The cork is now fixed tightly into the tube, and a piece of paper, slightly longer than the tube, is moistened with carbon disulphide and placed within the tube, which is supported at an angle of about  $45^\circ$  by means of a clamp and retort stand. After a minute or so, the tube will be practically filled with the vapour of carbon bisulphide, and the paper may be withdrawn.

On passing a spark from a Ruhmkorff coil placed in connection with the wires running through the cork the fulminate explodes, and the internal walls of the tube are seen to be lined with a deposit of soot mixed with a small quantity of mercuric sulphide and free sulphur.

Similar effects are obtained by filling the tube with a mixture of carbon disulphide vapour and nitrogen or carbon dioxide, and then passing the spark. In these cases the deposit of carbon is comparatively dense, lustrous, and coherent.

Only a very small quantity of mercuric fulminate is required to initiate the decomposition, and this fact serves to support Berthelot's theory of the nature of the change. The shock of the explosion communicates to the layer of the gaseous molecules in immediate proximity to the fulminate an enormous active force, whereby the "molecular edifice" is shaken to pieces, and the initial active force is augmented to a degree corresponding to the heat evolved by the decomposition of the gas. A new shock is thereby produced in the next layer, and the action is repeated and so propagated until the molecular system is completely destroyed (compare Berthelot, *Bull. Soc. Chim.*, **38**, 5—8).

Attempts to bring about this decomposition by the use of other explosive agents than the yellowish-brown powder and the fulminates have not hitherto been successful. Mr. G. S. Newth, my lecture assistant, has tried for me the action of gunpowder, mixtures of potassium chlorate and phosphorus, of potassium chlorate and ammonium picrate, acetylide of copper, diamine diiodide (iodide of nitrogen), Berthollet's detonating silver, mixtures of oxygen and hydrogen, oxygen and carbon disulphide vapour—all of which may be fired by the electric spark, but the explosion of these agents has apparently no decomposing effect on the carbon disulphide vapour. A minute fragment of the yellowish-brown powder placed in a tube filled with carbon disulphide vapour and rubbed with a glass rod exploded with great violence, and occasioned an abundant deposit of carbon and sulphur on the walls of the tube. It appeared as if the free sulphur existed for some little time as a gas, for it was mainly deposited in the upper portion of the tube, whereas the great bulk of the carbon settled near the bottom.

As to the nature of the yellowish-brown powder, I am as yet only able to offer conjectures. It may be a compound of carbon monosulphide and potassium, analogous to that formed by the action of carbon monoxide and potassium. There is some ground for the belief that the highly explosive character of the latter substance is really due to the formation of potassium acetylide produced by the action of moist air upon it. That the compound of carbon monoxide and potassium, when thrown into water, detonates with great violence

and with the evolution of acetylene is well known; indeed it was by this action that John Davy first isolated acetylene. In the case of the compound formed by the action of carbon bisulphide, there can, however, be no suspicion of the presence of hydrogen.

## XXIX.—*Some Compounds of Tribenzylphosphine Oxide.*

By NORMAN COLLIE, Ph.D., F.R.S.E.

IN a paper by Professor Letts and myself, "On the Action of Phosphide of Sodium on Haloïd Ethers and on the Salts of Tetrabenzylphosphonium" (*Trans. Roy. Soc. Edin.*, **30**, Part 1, 181), we showed how the oxide of tribenzylphosphine could be easily obtained from chloride of tetrabenzylphosphonium; and some of its compounds were prepared. In this paper the action of nitric acid and sulphuric acid on oxide of tribenzylphosphine will be described, and also the combinations it forms with hydrogen chloride and with acetyl chloride.

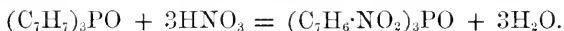
The oxides of tertiary phosphines belong to a somewhat remarkable class of compounds. They are amongst the most stable substances to be met with in the whole range of organic chemistry; they are usually unacted on by such reagents as sodium, fuming nitric acid, and pentachloride of phosphorus, they are neutral in their action on litmus-paper, yet they unite with acids, such as hydrochloric or hydrobromic acid, with the greatest ease to form well-characterised compounds; and they also combine with metallic chlorides, iodides, &c., forming double salts, an excellent example of which is the beautifully crystalline compound which triethylphosphine oxide forms with zinc iodide,  $2(\text{C}_2\text{H}_5)_3\text{PO}, \text{ZnI}_2$ , first obtained by Hofmann; and although no definite combination of a phosphine oxide with a base is known, yet if strong caustic soda be added to an aqueous solution of triethylphosphine oxide, an oily layer separates which contains a very large quantity of sodium hydroxide, and which may possibly be a definite compound of the two.

I have now prepared compounds which show that in certain cases the phosphine oxides may also be compared with hydrocarbons, as they yield sulphonic acids and nitro-derivatives when treated with sulphuric acid or nitric acid. The study of these combinations of the oxides of the tertiary phosphines with acids, salts, and other substances, does not at first sight appear to be of much interest, owing to our inability to express the resulting formulæ of the compounds

graphically, unless phosphorus be taken as more than pentavalent; yet the great stability of some of the compounds formed makes this study one of interest, and certainly seems to point to the combination being something more definite than that which occurs in the case of ordinary double compounds, which are easily decomposed when dissolved or by heating. For example, when gaseous hydrogen bromide is passed into melted oxide of triethylphosphine, it is absorbed with the evolution of much heat, and a definite crystalline substance is formed, which distils constantly at a temperature as high as  $303\text{--}308^\circ$  (Letts, *Trans. Roy. Soc. Edin.*, **30**, Part 1, 332), and which has the formula  $4(\text{C}_2\text{H}_5)_3\text{PO}, 3\text{HBr}$ . This compound, even when distilled under reduced pressure, contains identically the same amount of hydrogen bromide. Again, all oxides of tertiary phosphines form well-marked platinochlorides of the unusual formula  $4\text{R}_3\text{PO}, \text{H}_2\text{PtCl}_6$ , although the compound of the oxide itself with hydrogen chloride is analogous to the hydrogen bromide compound, and has the formula  $4\text{R}_3\text{PO}, 3\text{HCl}$ .

Some of the combinations of tribenzylphosphine oxide have already been prepared by Professor Letts and myself. The platinochloride,  $4(\text{C}_7\text{H}_7)_3\text{PO}, \text{H}_2\text{PtCl}_6$ , and also a compound with bromine,  $5(\text{C}_7\text{H}_7)_3\text{PO}, 4\text{Br}_2$ , were obtained, and a sulphur compound,  $5(\text{C}_7\text{H}_7)_3\text{PO}, \text{S}$ , was produced by heating the oxide with flowers of sulphur. Fleissner (*Ber.*, **13**, 1665) has also prepared a large number of double compounds of the oxide with metallic salts.

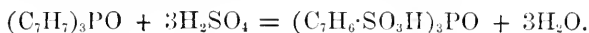
During my experiments with tribenzylphosphine oxide I have found it to be one of the least stable of this class of compounds. When fused with sodium, the oxygen is certainly removed from the molecule, but owing to the high temperature further decomposition occurs. It can also be partially oxidised to phosphoric acid, when boiled with fuming nitric acid and chlorate of potassium, or when warmed with a strong alkaline solution of permanganate of potassium. Chromic acid is, however, without action on it. It dissolves readily in warm oil of vitriol without change, but if fuming nitric acid be carefully added to this solution a trinitro-derivative is produced,



This nitro-compound is oxidised by permanganate of potassium, yielding paranitrobenzoic and phosphoric acids, thus showing that the nitro-groups are in the para-position.

The trinitro-compound, when treated with tin and fuming hydrochloric acid, is probably reduced to a triamido-derivative, which does not seem to form salts, it is, therefore, not of a basic character, and is unlike the corresponding derivative obtained by Michaelis and H. v. Soden (*Ber.*, **17**, 921) from the oxide of triphenylphosphine.

The oxide of tribenzylphosphine when dissolved in warm sulphuric acid is reprecipitated on diluting the solution with water, but if the mixture be heated to 150—170°, and water added when it is cold, the solution remains clear and contains a sulphonic acid,



This acid forms a soluble barium salt, from which the acid can be obtained. The aqueous solution of the acid evaporated in a vacuum dries up to a semi-crystalline mass. In this case also, the new groups taken up by the molecule are in the para-position, for on oxidation parasulphobenzoic acid is obtained.

Tribenzylphosphine oxide greedily absorbs gaseous hydrogen chloride, forming a compound,  $4(\text{C}_7\text{H}_7)_3\text{PO}\cdot 3\text{HCl}$ , but this is unstable, and when heated parts with hydrogen chloride.

Acetyl chloride also unites with the oxide, giving a compound,  $(\text{C}_7\text{H}_7)_3\text{PO}\cdot\text{CH}_3\cdot\text{COCl}$ . This substance also dissociates when heated.

*The Action of Nitric Acid on Tribenzylphosphine Oxide.*

Some pure oxide of tribenzylphosphine was dissolved in strong sulphuric acid, care being taken not to allow the temperature to rise; excess of strong nitric acid was then carefully added, and the whole poured into water. A white, flocculent precipitate was obtained, which was washed with water, dissolved in hot glacial acetic acid, and again precipitated by water. Thus prepared it formed a white, amorphous substance, which scarcely showed any signs of crystallisation. On heating, it melts at about 100°, and at higher temperatures suddenly deflagrates, leaving a mass of carbon. An analysis gave the following results:—

- I. 0.311 gram substance gave 0.626 gram  $\text{CO}_2$  and 0.101 gram  $\text{H}_2\text{O}$ .  
 II. 0.487 gram substance gave 38.2 c.c. of nitrogen at 13° and 745 mm. pressure.

	Found.		Calculated for $(\text{C}_7\text{H}_6\cdot\text{NO}_2)_3\text{PO}$ .
	I.	II.	
C .....	54.89	—	55.38
H.....	3.60	—	3.95
N.....	—	9.07	9.23

The trinitro-derivative of the oxide remains unchanged when boiled with chromic acid, but a warm alkaline solution of permanganate of potassium oxidises it at once. On the addition of an acid to this solution, a white, crystalline precipitate separates immediately.

This by recrystallisation from dilute alcohol may be obtained in the form of leafy plates melting at  $231^{\circ}$ . It is acid to litmus-paper. It was converted into the silver salt and analysed.

0.230 gram salt gave 0.0920 Ag = 40.0 per cent. Ag.

Theory for  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{COOAg}$  = 39.4      „

The melting point of paranitrobenzoic acid is  $234^{\circ}$  uncorrected, thus showing without doubt that the crystals obtained were that substance.

Some of the trinitro-derivative was warmed with strong hydrochloric acid and tin. It slowly dissolved, and after the solution had been freed from tin by sulphuretted hydrogen a white, flocculent precipitate was obtained on the addition of sodium hydroxide. Several attempts were made to obtain this substance in a state of purity, but without success; the analyses did not agree amongst themselves nor with the numbers required for a triamido-derivative of the oxide, but as the substance no longer deflagrated when heated, it certainly was not the original nitro-derivative.

#### *Action of Sulphuric Acid on Tribenzylphosphine Oxide.*

The oxide when dissolved in strong sulphuric acid does not react unless the temperature be raised above  $100^{\circ}$ ; between  $150^{\circ}$  and  $170^{\circ}$  the whole of the oxide is readily converted into a sulphonic acid. This acid is soluble in water, and can be separated from the excess of sulphuric acid (in the form of a soluble barium salt) by the addition of barium hydroxide. The acid itself is semi-crystalline, and dries up to a syrup over sulphuric acid. The barium salt is also soluble in water and uncrystallisable, but can be obtained pure by the evaporation of an aqueous solution. The silver salt is thrown down as a flocculent, white precipitate when a strong solution of the barium salt is added to nitrate of silver. The copper salt is green in colour and soluble in water; the lead salt is also soluble.

An analysis of the barium salt gave the following results:—

0.5905 gram salt dried at  $120^{\circ}$  gave 0.200  $\text{BaSO}_4$  = 19.9 per cent. Ba.

This agrees with the amount of barium required by the monacid salt  $(\text{C}_7\text{H}_6\cdot\text{SO}_3)_2\text{Ba}(\text{C}_7\text{H}_6\cdot\text{SO}_3\text{H})\text{PO}$ , which is 19.9 per cent. Ba, while the amount of barium contained in the normal salt  $(\text{C}_7\text{H}_6\cdot\text{SO}_3)_6\text{Ba}_3\text{P}_2\text{O}_2$  is 26.9 per cent. Ba.

A determination of sulphur was also made in the barium salt.

0.422 gram salt gave 0.410 gram  $\text{BaSO}_4$  = 13.6 per cent. S.

Calculated for  $(\text{C}_7\text{H}_6\cdot\text{SO}_3)_2\text{Ba}(\text{C}_7\text{H}_6\cdot\text{SO}_3\text{H})\text{PO}$  = 13.8      „

The sulphonic acid, like the nitro-compound, is not oxidised by chromic acid solution, but it is when warmed with an alkaline solution of permanganate of potassium. The acid obtained from this solution crystallises in needles, which decompose when heated to  $190^{\circ}$ . Whether they were parasulphobenzoic acid or not it is impossible to say with certainty, owing to the small amount under examination. But parasulphobenzoic acid melts at  $200^{\circ}$  with decomposition.

*Action of Hydrogen Chloride on Tribenzylphosphine Oxide.*

When warmed with an aqueous solution of hydrogen chloride, the oxide remains unchanged, but if a current of the dry gas be passed over the finely powdered oxide, it is readily absorbed, and a compound is obtained which is unchanged when exposed to the air. It decomposes into tribenzylphosphine oxide and hydrogen chloride when heated or when boiled with water.

0.5955 gram salt took 13.0 c.c.  $\text{AgNO}_3$  decinormal solution =  
7.7 per cent. Cl.

Theory required by  $4(\text{C}_7\text{H}_7)_3\text{PO}, 3\text{HCl} = 7.6$  per cent. Cl.

A similar compound is formed when hydrogen bromide is used.

If acetyl chloride be added to a solution of the oxide in acetic acid, and the solution be slowly evaporated, a crystalline salt will separate out, which is a definite compound of acetyl chloride and the oxide. It is decomposed by boiling water or by solution of sodium hydroxide, and when heated it splits up into acetyl chloride and the oxide.

On analysis, it gave the following result:—

0.601 gram salt took 15.0 c.c.  $\text{AgNO}_3$  decinormal = 8.8 p. c. Cl.

Calculated for  $(\text{C}_7\text{H}_7)_3\text{POCH}_3\cdot\text{COCl} = 8.9$  „

XXX.—*The Constitution of Primuline and Allied Sulphur Compounds.*

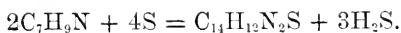
By ARTHUR G. GREEN, F.I.C.

In February, 1887, I found that by heating paratoluidine with sulphur in the proportion of from 4 to 5 atoms of the latter to 2 mols. of the former, a product was obtained which consisted of a mixture of at least two bases containing sulphur. The sulphonic acid of the more complex of these two bases had the peculiar property of dyeing

unmordanted cotton primrose-yellow, and was capable of being diazotised within the fibre, and of combining with amines and with phenols. This product was put upon the market by Messrs. Brooke, Simpson, and Spiller, Limited, under the name of "Primuline" (*Journ. Soc. Chem. Ind.*, 1888, 179), and is largely employed in cotton dyeing on account of the great range of fast shades that may be obtained with it. It now appears in the market under a variety of names, such as "polychromine," "thiochromogen," "sulphine," "aureoline," "chamaeleon-yellow," "carnotine," &c. Since the discovery of the peculiar behaviour of paratoluidine with sulphur, I have been constantly engaged in attempting to elucidate the very complicated reactions which take place; and although I have not yet been able to determine with certainty the formula of primuline, I have gained considerable insight into the constitution of the entirely new class of compounds to which it belongs. Any incompleteness in the present work must be excused, on the ground that its publication has been hastened by the recent appearance in the *Berichte* of researches on the same subject, in which some of my results have been forestalled.

*Action of Sulphur on Paratoluidine.*

In 1872, Merz and Weith (*Ber.*, 4, 393) showed that by heating paratoluidine with sulphur in presence of oxide of lead, thioparatoluidine (diamidoditolyl sulphide)  $[C_6H_3(CH_3) \cdot NH_2]_2S$ , was obtained, but since that time no other investigation has been published on the subject. When oxide of lead is not employed, no reaction takes place at  $140^\circ$ , but at a higher temperature,  $175^\circ$  and upwards, hydrogen sulphide is evolved freely, and the reaction takes quite a different course. By heating 2 mols. of paratoluidine with 4 atoms of sulphur for about 10 hours, the loss of hydrogen sulphide corresponds exactly with the equation—



The product is not homogeneous, but consists of about 50 per cent. of a base,  $C_{14}H_{12}N_2S$  (dehydrothiotoluidine), 40 per cent. of primuline-base, and 10 per cent. of unaltered paratoluidine. If a smaller proportion of sulphur is employed, a large quantity of the toluidine remains unaltered, whilst the dehydrothiotoluidine,  $C_{14}H_{12}N_2S$ , is still the main product, accompanied by a greatly diminished amount of primuline base and a certain quantity of thiotoluidine.

*Dehydrothiotoluidine,  $C_{14}H_{12}N_2S$ .*

Several methods can be employed for the isolation of this base, the most convenient being the extraction of the melt by boiling it with



hydrochloric acid diluted with  $1\frac{1}{2}$  times its bulk of water, precipitating the base with caustic soda, distilling it, and finally crystallising from amyl alcohol. By this method a very good yield of the pure base is obtained, whereas, if crystallisation alone is employed, without previously distilling, a pure product can only be obtained with difficulty and in small quantity. Another convenient method of isolating the base consists in employing twice the theoretical quantity of toluidine, and mixing the warm melt with benzene and light petroleum: on cooling, the dehydrothiotoluidine crystallises out, whilst the thiotoluidine and excess of paratoluidine remain in solution.

On analysis the base gave the following numbers:—

	Calculated for $C_{14}H_{12}N_2S$ .	Found.		
		I.	II.	III.
S .....	13.36	13.28	13.64	13.77

The dehydrothiotoluidine is a most beautiful compound: it crystallises from amyl alcohol in long, yellowish, iridescent needles; it melts at  $191^\circ$  (uncorr.), and boils with very little decomposition at  $434^\circ$  (uncorr.) under 766 mm., B.P. It is very soluble in acetic acid, tolerably soluble in hot amyl alcohol, less readily in hot ethyl alcohol, and only sparingly in benzene; in boiling water, it dissolves to the extent of about 1 part in 20,000. Its alcoholic and aqueous solutions have a beautiful violet-blue fluorescence, which also characterises all its derivatives. It dissolves in hydrochloric acid, forming the dihydrochloride, and on adding water a yellow precipitate of the monohydrochloride is formed. Dehydrothiotoluidine is a very stable compound: its sulphur cannot be removed or displaced by any of the usual reactions for removing sulphur from organic sulphides.

When absorbed by the skin, it produces, in certain people, severe irritation, resembling eczema, an observation which has also been made by Hofmann with regard to several other sulphur compounds. When boiled with zinc-dust and hydrochloric acid, it is reduced to a base of totally different properties which I have not yet had time to investigate. On distillation with zinc-dust (10 parts), paratoluidine is regenerated. When heated with more sulphur, it gives primuline-base. By titrimetric diazotisation, using starch and potassium iodide as an indicator, it gave the following numbers, which prove it to contain only one  $NH_2$ -group:—

	Calculated for $C_{14}H_{10}SN \cdot NH_2$ .	Found.		
		I.	II.	III.
Weight of $NaNO_2$ corresponding to 1 gram of base .....	0.287	0.29	0.30	0.31

That the other nitrogen atom has no hydrogen directly united to it was proved by the fact that the base can only form a monacetyl-derivative. The diazochloride is readily soluble in water, forming an orange-yellow solution, which is perfectly stable at ordinary temperatures; the diazosodium sulphite is insoluble. By combination of the diazo-compound with sulphonic acids of  $\alpha$ - and  $\beta$ -naphthylamine, azo-colours are produced which are capable of dyeing unmordanted cotton from an alkaline bath, a property which has hitherto only been observed in azo-compounds derived from diamido-compounds.

*Acetyldehydrothiotoluidine*,  $C_{14}H_{10}SN \cdot NH \cdot CO \cdot CH_3$ .

This compound was prepared by boiling a strong acetic acid solution of the base with excess of acetic anhydride. It forms small, white prismatic crystals which melt at  $227^\circ$  (uncorr.). It is sparingly soluble in acetic acid, almost insoluble in alcohol. On hydrolysis with sulphuric acid, distillation, and titration of the acetic acid formed, it gave:—

	Calculated for $C_{14}H_{10}SN \cdot NH \cdot CO \cdot CH_3$ .	Found.
$C_2H_3O$ .....	15.25	15.76

The acetyl-derivative combines with bromine to form an unstable addition-product; this separated as a yellow precipitate on adding bromine to an acetic acid solution of the acetyldehydrothiotoluidine. It is a very unstable compound, evolving bromine when heated, and even on boiling with water.

*Dimethyldehydrothiotoluidine*,  $C_{14}H_{10}SN \cdot N(CH_3)_2$ .

This compound was prepared by heating dehydrothiotoluidine with methyl iodide, or by heating the hydrochloride with methyl alcohol at  $120$ – $150^\circ$ . It forms yellowish-white, flattened needles or plates, somewhat sparingly soluble in alcohol. It melts at  $196$ – $197^\circ$ , and boils at about the same temperature as dehydrothiotoluidine. It dissolves readily in strong hydrochloric acid, forming a light yellow solution of the dihydrochloride, which is decomposed on addition of water with formation of a yellow precipitate of the monohydrochloride.

The *trimethylammonium iodide* and *chloride*,  $C_{14}H_{10}SN \cdot N(CH_3)_3I$  and  $C_{14}H_{10}SN \cdot N(CH_3)_3Cl$ , are very remarkable, as they possess strong tinctorial powers. They are formed together with the dimethyl-derivative by heating dehydrothiotoluidine with methyl iodide and methyl alcohol, or with methyl alcohol and hydrogen chloride at  $150$ – $200^\circ$ . The chloride and iodide are bright yellow powders,

readily soluble in water to yellow solutions, from which wool, silk, and cotton, mordanted with tannin, are dyed a pure yellow of exactly the same shade as auramine. The colour on silk has a beautiful green fluorescence. The aqueous solution of the chloride gave with platinic chloride a crystalline orange precipitate of the platinochloride  $[C_{14}H_{10}SN \cdot N(CH_3)_3Cl]_2PtCl_4$ . The platinochloride melts with decomposition at  $231-234^\circ$ , and on ignition gave the following numbers:—

	Calculated for $[C_{14}H_{10}SN \cdot N(CH_3)_3Cl]_2PtCl_4$ .	Found.	
		I.	II.
Pt .....	20.02	20.19	20.02

On heating the iodide it melts with evolution of methyl iodide, leaving a residue of dimethyldehydrothiitoluidine,  $C_{14}H_{10}SN \cdot N(CH_3)_2$ . The yellow solutions of the iodide and chloride are nearly decolorised on adding an excess of mineral acid, probably from formation of di-acid salts; on dilution, the yellow colour returns. The solutions of the iodide and chloride give a white, flocculent precipitate of the hydroxide on adding caustic soda; this redissolves in excess, forming a colourless solution (probably the natroxide,  $C_{14}H_{10}SN \cdot N(CH_3)_3ONa$ ). From the alkaline solution, the hydroxide is again precipitated on neutralisation with carbonic acid or acetic acid. The freshly precipitated hydroxide is readily soluble in dilute mineral acids with production of bright yellow crystalline salts. If the hydroxide is dried for a few hours at  $80-90^\circ$ , it entirely changes its properties, being converted into the dimethyldehydrothiitoluidine, melting at  $197^\circ$ , described above.

*Dehydrothiitoluidinemonosulphonic Acid*,  $C_{14}H_9SN(NH_2) \cdot SO_3H$ .

This sulphonic acid was prepared by slowly adding sulphuric anhydride (containing 70 per cent. of free  $SO_3$ ) to a solution of dehydrothiitoluidine in 5 parts of ordinary sulphuric acid, keeping the temperature below  $50^\circ$ . The solution was poured into cold water, and the insoluble sulphonic acid collected and washed. It was then suspended in boiling water and neutralised with ammonia, when the sparingly soluble ammonium salt crystallised out; the yield was nearly theoretical.

On analysis, the dry ammonium salt gave the following numbers:—

	Calculated for $C_{14}H_9SN(NH_2) \cdot SO_3NH_4$ .	Found.		
		I.	II.	III.
S .....	18.9	18.56	18.7	18.58

By titrimetric diazotisation the following numbers were obtained:—

	Calculated for $C_{14}H_9SN(NH_2) \cdot SO_3 \cdot NH_4$ .	Found.
Weight of $NaNO_2$ corresponding to } 1 gram of the sulphonate . . . . . }	0.205	0.210

The free acid was obtained well crystallised on adding acetic acid to a hot ammoniacal solution and allowing it to cool. It is sparingly soluble in hot, insoluble in cold water. It crystallises either in flattened, yellow needles (with 1 mol.  $H_2O$ ), or in aggregated, orange leaflets (with 2 mols.  $H_2O$ ). On drying, at  $120^\circ$  the yellow acid lost:—

	Calculated for $C_{14}H_9SN(NH_2) \cdot SO_3H + H_2O$ .	Found.
$H_2O$ . . . . .	5.32	4.7

At the same temperature the orange acid lost—

	Calculated for $C_{14}H_9SN(NH_2) \cdot SO_3H + 2H_2O$ .	Found.
$H_2O$ . . . . .	10.11	10.13

A determination of the molecular weight of the dry acid by titration with normal sodium carbonate gave the following result:—

	Calculated for $C_{14}H_9SN(NH_2) \cdot SO_3H$ .	Found.
Mol. wt. . . . .	320	322.6

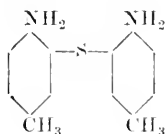
As this sulphonic acid is the lowest that could be obtained, the molecular weight of the dehydrothiitoluidine and its derivatives is established.

The salts of the sulphonic acid are mostly colourless, and tolerably soluble in water, to which they impart a violet-blue fluorescence. They have no affinity for cotton, differing in this respect from the sulphonic acid of the primuline-base. The most characteristic salts are the ammonium and cupric salts. The former crystallises in small, colourless plates (with 1 mol.  $H_2O$ ), which are sparingly soluble in hot water, very sparingly in cold water. The cupric salt is an insoluble reddish-brown precipitate, closely resembling cupric ferrocyanide; it is formed on adding copper sulphate to a soluble salt of the acid. The silver salt is an insoluble, white precipitate.

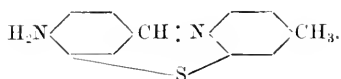
#### *Constitution of Dehydrothiitoluidine.*

From the foregoing, it is established that the base has the formula  $C_{14}H_{10}SN \cdot NH_2$ . The first product of the action of sulphur on

paratoluidine is undoubtedly Merz and Weith's thiotoluidine (diamidoditoly sulphide):—



By the further action of sulphur on this compound, 4 atoms of hydrogen are removed, with formation of dehydrothiotoluidine. Since one nitrogen of the latter is nitrilic in character, whilst the other is in the form of  $\text{NH}_2$ , it follows that of the 4 atoms of hydrogen eliminated two must have come from an  $\text{NH}_2$ -group, and the other two from a methyl or a benzene nucleus. That the condensation has not taken place between two carbon-atoms is also proved by the fact that paratoluidine is regenerated on distillation with zinc-dust. The fact that the base is capable of combining with hydrogen or bromine indicates the existence of an unsaturated double union, whilst the instability of the bromine compound (see acetyl-derivative) confirms the conclusion that it is carbon and nitrogen that are doubly connected. This is only possible on the assumption that the condensation has taken place by the removal of the four hydrogen-atoms from an  $\text{NH}_2$ - and  $\text{CH}_3$ -group; for if the nuclear hydrogen were involved the compound would not be unsaturated, and, moreover, would be scarcely likely to give paratoluidine on distillation with zinc-dust. The constitution of the base must, therefore, be represented by the formula



This formula entirely agrees with all the reactions of the substance, and with the fact that analogous compounds can only be obtained from primary bases containing methyl; thus aniline, when similarly treated, gives diamidodiphenyl sulphide. The great stability of dehydrothiotoluidine and its derivatives, and the impossibility of removing or displacing the sulphur by ordinary means, appears to be due to the presence of a ring of six carbon-atoms, nitrogen and sulphur.

#### *Primuline-base.*

This compound is formed, together with dehydrothiotoluidine, when paratoluidine (2 mols.) is heated with 4 to 5 atoms of sulphur. It is also obtained by heating thiotoluidine or dehydrothiotoluidine with more sulphur, and hence these compounds must be interme-



The difference between dehydrothiitoluidine and its more condensed derivative—primuline—in the affinity for cotton and tinctorial power of the latter, is probably due to the increase of molecular weight, for both these properties are possessed by the dehydrothiitoluidine in an incipient state, as is shown by the fact that the quaternary ammonium salts are strong colouring matters, whilst the corresponding azo-colours have a strong affinity for unmordanted cotton.

The condensation of paratoluidine by sulphur does not appear to come to a stop at primuline-base, but seems to proceed further with production of still more complicated compounds of extremely high melting point.

I shall continue the investigation, and hope soon to obtain further light on these remarkable reactions.

In conclusion, I have to express my thanks to Messrs. Brooke, Simpson, and Spiller, Ltd., in whose laboratory the above investigation was performed, and to Mr. F. Evershed for much valuable assistance. The sulphur estimations were kindly made by Dr. R. T. Plimpton by his new method.

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### XXXI.—*Contributions to the Knowledge of Citric and Aconitic Acids.*

By SIDNEY SKINNER, B.A., late Scholar of Christ's College, Cambridge,  
and S. RUHEMANN, Ph.D., M.A.

THE compounds formed by the action of aniline on citric and aconitic acids have been carefully examined by Pebal (*Annalen*, **82**, 78; **98**, 67). In the first paper he deals with the direct action of aniline on citric acid, and describes several of the anilides and anils produced. The second paper gives an account of a substance which he calls "oxychloreitronsäure" (chlorocitryl monochloride), from which he obtained an aconityl-derivative by the action of aniline.

In the course of some experiments, having occasion to prepare the chlorocitryl monochloride with the view of testing some results previously obtained by one of us, it seemed desirable to submit it to a more complete examination, and with this object we have reviewed the action of primary monamines on citric acid.

Pebal's directions for the preparation of the chlorocitryl monochloride were followed as closely as possible; three equivalents of phosphorus pentachloride mixed with one of citric acid (dried at 130°) were shaken together in a flask; the heat evolved in the

reaction caused the mass to become gradually pasty, and, on slightly warming, the mixture was transformed into a light-red liquid. Overheating on the water-bath must be avoided, or else the colour will become dark and decomposition begin. If the light-red liquid is poured off from the excess of pentachloride and mixed with dry carbon bisulphide, crystalline needles of the citric acid chloride separate out in a few minutes. These are collected on a filter, washed with dry carbon bisulphide until they are as free as possible from phosphorus oxychloride, pressed, and dried in a vacuum over caustic potash and sulphuric acid.

The chlorocitryl monochloride thus obtained is a hard, white substance, exhibiting no crystalline structure when dried, insoluble in carbon bisulphide, but readily soluble in benzene, and melting at about  $100^{\circ}$ . In moist air, it rapidly absorbs water with evolution of hydrogen chloride.

Pebal analysed the substance by an indirect method, and the results led him to the conclusion that the formula  $C_{12}H_6O_{12}Cl_2$  ( $C = 6$ ,  $O = 8$ ) best represented its composition. This cannot, however, be reconciled with the present view of the constitution of citric acid or with the reactions which Pebal attributed to it. Its composition may, however, be expressed by the formula  $C_6H_6O_5Cl_2$ , which requires the percentage composition—

C <sub>6</sub> .....	72	31.4
H <sub>6</sub> .....	6	2.6
O <sub>5</sub> .....	80	35.0
Cl <sub>2</sub> .....	71	31.0
	<hr/>	<hr/>
	229	100.0

This agrees as well with Pebal's analyses as with ours. We have determined the chlorine in several specimens of the product with such varied results as 19.92, 21.72, 25.96 per cent., and in a specimen recrystallised from benzene without heating, and dried in a vacuum, we found 29.6 per cent. This still contained minute traces of phosphorus, but was decidedly the purest specimen, and agrees best with the assumption that the compound is a chlorocitryl monochloride. As the substance could not be obtained pure enough for ultimate analysis, it was evident that its composition could only be arrived at by the study of its reactions.

#### *Action of Water on Chlorocitryl Monochloride.*

On addition of water, it readily dissolves if impure, but after recrystallisation from benzene it is necessary to warm slightly before



it dissolves. An aqueous solution of the crude substance was evaporated to dryness on a water-bath, and the crystalline residue, which was found to be free from chlorine, was shaken with ether. The soluble portion left on evaporation of the ether was dissolved in alcohol and saturated with hydrogen chloride; on adding water, an oil separated, which boiled at about  $294^{\circ}$ . Analysis proved it to be ethyl citrate.

	Calculated for $C_{12}H_{20}O_7$ .	Found.	
		I. B. p. $294^{\circ}$ C. at ordinary pressure.	II. B. p. $218^{\circ}$ C. at 75 mm. pressure.
C.....	52.1	52.1	51.6
H.....	7.2	7.24	7.2

The larger portion of the substance which was not taken up by ether was recrystallised from water. Analysis of these crystals dried in a vacuum gave numbers corresponding with those required for citric acid.

	Calculated for $C_6H_8O_7 + H_2O$ .	Found.
C .....	34.28	34.6
H .....	4.76	5.1

Hence citric acid is the only product of the action of water on chlorocitryl monochloride.

#### *Action of Heat on Chlorocitryl Monochloride.*

The crude substance when heated to  $125^{\circ}$  melts and gives off hydrogen chloride. The resulting product was dissolved in water, the solution evaporated to dryness, and the crystalline residue shaken with dry ether. This extracted a crystalline acid, the silver salt of which gave on analysis 65.33 per cent. of silver. It is therefore silver aconitate, which requires 65.45 per cent. Ag. Hence the action of heat on chlorocitryl monochloride results in the formation of aconityl chloride, which under the influence of water is transformed into aconitic acid. The darkening which, as above mentioned, follows prolonged heating in the preparation of chlorocitryl monochloride, is undoubtedly due to a partial change into aconityl chloride, for aconitic acid may be readily obtained by the action of water on the darkened liquid.

#### *Action of Aniline on Chlorocitryl Monochloride.*

On the gradual addition of the finely powdered acid chloride to aniline, a violent reaction takes place, causing a considerable rise of temperature, and a resinous mass is produced, which melts on heating

and only partially solidifies on cooling. This contains aconityl anil-anilide, which may be best extracted by first distilling with steam to remove the excess of aniline, and subsequently recrystallising the solid residue from methylated spirit. The anil-anilide forms small needles of a faintly yellow colour, insoluble in water and ether, and only slightly soluble in alcohol. It appears to suffer decomposition at about  $200^{\circ}$ , but for complete fusion requires a higher temperature, given as  $250^{\circ}$  by Michael (*Amer. Chem. J.*, **9**, 192), for a specimen prepared from aconitic acid.

The formula  $C_{15}H_{14}N_2O_3 = C_6H_5 \cdot N < \begin{matrix} CO \cdot CH \\ || \\ CO \cdot C \cdot CH_2 \cdot CO \cdot NH \cdot C_6H_5 \end{matrix}$  requires the following numbers:—

	Theory.		Found.			
			I.	II.	III.	IV.
C <sub>15</sub> .....	216	70.59	70.24	70.30	—	—
H <sub>14</sub> .....	14	4.57	4.99	5.23	—	—
N <sub>2</sub> .....	28	9.15	—	—	9.24	9.47
O <sub>3</sub> .....	48	15.69	—	—	—	—
	306	100.0				

This substance was described by Pebal, who prepared it from chlorocitryl monochloride, as well as from aconitic acid. It is evident that its formation from the former is due to removal of hydrogen chloride as aniline hydrochloride, with conversion of the citryl radicle into the aconityl radicle.

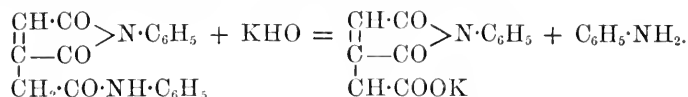
*Action of Alkalis on Aconityl Anil-anilide.*

Strong or dilute solutions of potassium hydroxide, and even of ammonia, decompose aconityl anil-anilide with formation of aniline and the salt of an acid. The anilide dissolves in the alkali after slight warming, forming a red liquid with a violet fluorescence. On addition of dilute mineral acids to the concentrated solution, a precipitate of the acid is thrown down; this may be purified by shaking with ether, in which it is only sparingly soluble. On evaporating the ether, the crystalline acid is left contaminated with a green viscous substance; the latter may, however, be readily got rid of by treatment with ether, in which it is very easily soluble. The acid crystallises from alcohol in rosettes of a faintly yellow colour, which melt at  $250^{\circ}$  with decomposition.

Analysis proved it to be aconitylanilcarboxylic acid. Its formula,  $C_{12}H_9NO_4$ , requires—

	Calculated.	Found.	
		I.	II.
N .....	6.06	6.83	6.27

and the following equation represents its formation—



Aconitylanilcarboxylic acid is but sparingly soluble in water. Its aqueous solution reddens litmus-paper, and the addition of alkali produces a violet fluorescence. With silver nitrate, the ammonium salt of the acid yields a silver salt, which is, however, very unstable, and on warming gently deposits a silver mirror. Dried in a vacuum, it gave on analysis 31.5 per cent. of silver, whilst  $\text{C}_{12}\text{H}_8\text{AgNO}_4$  requires 31.9 per cent. Ag.

This acid is doubtless identical with the acid prepared by Pebal by the action of phosphorus pentachloride on citrylanilcarboxylic acid, for it has been shown that phosphorus trichloride when heated with ethyl citrate transforms it into ethyl aconitate (Conen, *Ber.*, **12**, 1655). Aconitylanilcarboxylic acid is closely related to pyrrol, for when distilled with zinc-dust it readily yields a liquid which possesses the characteristic odour of pyrrol, and gives a bright scarlet colour to a pine-chip moistened with strong hydrochloric acid.

*Action of Orthotoluidine on Chlorocitryl Monochloride.*

By using orthotoluidine in place of aniline, we obtain a precisely analogous series of derivatives. Thus the product of their direct interaction is aconityltoluidtoluidide, a straw-yellow, crystalline substance melting at  $214^\circ$ , insoluble in water and ether and sparingly soluble in alcohol.

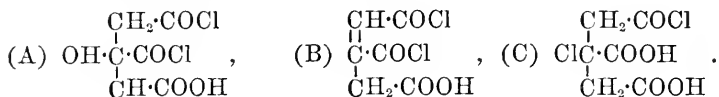
The formula  $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{N} < \begin{array}{c} \text{CO}\cdot\text{CH} \\ || \\ \text{CO}\cdot\text{C}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3 \end{array}$  requires—

	Calculated.	Found.
N .....	8.38	8.67

Here again the chlorocitryl radicle has been transformed into the aconityl radicle by the removal of hydrogen chloride by the toluidine with formation of orthotoluidine hydrochloride, which was identified both by its reactions and by analysis. Boiling potassium hydroxide solution dissolves aconityltoluidtoluidide, producing a strong violet fluorescence. Orthotoluidine is eliminated, and the potassium salt of aconityltoluidcarboxylic acid is formed, from which the acid may be precipitated by dilute hydrochloric acid. The toluidcarboxylic acid is soluble in water, and the addition of alkalis to the solution produces a fluorescence similar to that of the corresponding salts of the anilcarboxylic acid.

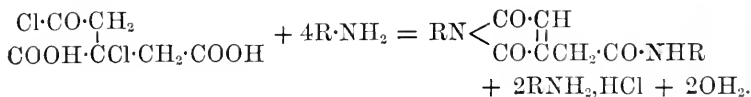
*Constitution of Chlorocitryl Monochloride.*

Taking into account the preparation of this substance, and the fact that analysis indicates that it contains two atoms of chlorine in its molecule, it would appear that its constitution might be represented by one of the three following formulæ:—



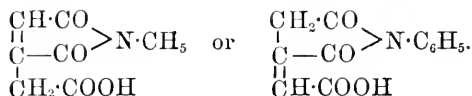
But the formula A, though accounting for the formation of citric acid by the action of water, would not readily explain the transformation into an aconityl-derivative, and on the other hand the formula B, though accounting for the latter fact, could not explain the former, as the conversion of aconitic into citric acid by the direct action of water has never been observed. Neither can the substance be a mixture of A and B, for then the action of water would give rise to both aconitic and citric acids, and that of aniline to both citryl and aconityl anil-anilides. The formula C alone expresses all the reactions that we have observed.

On heating to a temperature of 125° C., chlorocitryl monochloride splits into aconityl chloride and hydrogen chloride. From experiments made on the preparation of ethyl chlorocitrate, we have every reason to believe that this substance is formed by the interaction of equivalents of phosphorus pentachloride and ethyl citrate, but that on distillation in a vacuum it undergoes an analogous decomposition into ethyl aconitate and hydrogen chloride. We have, therefore, sufficient evidence that one of the chlorine-atoms of chlorocitryl monochloride is substituted for the alcoholic hydroxyl in citric acid, but it is not easy to ascertain which of the three acid hydroxyls is displaced by the other chlorine-atom. On treatment with aniline, the two unchanged carboxyl-groups first combine with it to form a salt which, however, readily loses water and gives rise to an anilide—a change which is very characteristic of aconitic, citraconic, itaconic, and maleic acids (Michael, *Amer. Chem. J.*, 9, 192). The equation representing the action of aniline and orthotoluidine on chlorocitryl monochloride may be given as follows:—

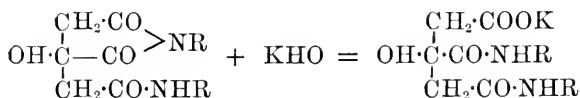


The fact of the formation of a pyrrol is a sufficient proof that the NR group unites with the carbon-atoms of adjacent carboxyls, for

if it united with those of the end carboxyls a pyridine-derivative would have been formed. Moreover, one of us has already proved (*Trans.*, **51**, 403) that the primary monamines such as methylamine cannot give rise by their action on ethyl acetyl citrate to substituted pyridines. The only question, therefore, remaining to be decided is whether the ethylene linking of the aconityl-group is within or without the pyrrol-ring. That is to say, which of the two following formulæ best represents aconityl anilcarboxylic acid :—



That the former is the correct one, results from the following considerations. The equation—

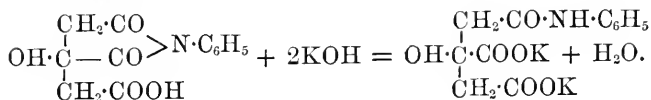


represents the general action of potassium hydroxide on citryl-derivatives of the formula  $\text{NR} < \begin{array}{c} \text{CO}\cdot\text{CH}_2 \\ \text{CO}\cdot\text{C}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHR} \end{array}$ .

Thus Pebal shows that citrylanil-anilide gives the potassium salt of citryldianilidocarboxylic acid :—



Analogous is the action of potassium hydroxide on the corresponding paratoluidine-compound (*Gill, Ber.*, **19**, 2352), on the  $\alpha$ - and  $\beta$ -naphthylamine-derivatives (*Hecht, Ber.*, **19**, 2614), and on the  $\psi$ -cumidine-compound (*Schneider, Ber.*, **21**, 660). Different, however, is the behaviour of aconitylanil-anilide towards potassium hydroxide, for in this case aniline is eliminated, and there is formed the potassium salt of aconitylanilcarboxylic acid, whilst, as shown by Pebal, citrylanilcarboxylic acid yields, under the influence of potassium hydroxide, citrylanilidocarboxylic acid,



This difference in behaviour can only be attributed to the ethylene linking of aconitic acid.

Ethyl aconitate has been shown by one of us (*Ber.*, 20, 3367) to be transformed by ammonia into a pyridine-derivative. The above considerations render it probable that in this reaction the ammonium salt of an imido-acid is also formed. We are therefore reinvestigating this reaction.

*University Laboratory, Cambridge.*

### XXXII.—*Action of Chloroform and Alcoholic Potash on Hydrazines.*

#### Part II.

By S. RUHEMANN, Ph.D., M.A.

IN a former communication made to the Society in conjunction with W. J. Elliott (*Trans.*, 1888, 850), it has been shown that the action of chloroform and alcoholic potash on phenylhydrazine is unlike that which takes place with the primary amines of the fatty and aromatic series.

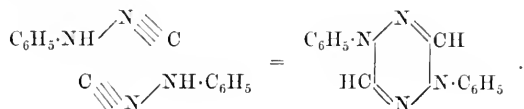
The product of the reaction, when freed from the unaltered base by means of dilute sulphuric acid, loses the odour of isonitrile after a short time, and is for the most part transformed into a very stable, odourless compound, which does not reduce Fehling's solution. The quantity of hydrazine transformed into this substance is, however, very small, if the operation is effected in the manner formerly described. After various attempts to improve the yield, I found that the most successful result was obtained when alcoholic potash was added to the solution of the base in chloroform and alcohol, instead of (as described in a former paper) adding chloroform to the solution of the base in alcoholic potash.

As already mentioned, a considerable quantity of resinous matter is formed in the preparation of this substance; the further examination of this resin shows that it contains a crystalline compound, which is very easily soluble in alcohol and ether, and can be extracted with boiling water. The aqueous solution, if decolorised by boiling with animal charcoal, yields colourless plates on cooling; these melt at 144°, and reduce Fehling's solution. This substance is formylphenylhydrazine, as in fact was found by a comparison with the product obtained by F. Just's method (*Ber.*, 19, 1201), and by a nitrogen determination, which gave—

	Theory for $C_6H_5 \cdot NH \cdot NH \cdot CHO.$	Found.
N .....	20.59	20.69

The formation of this compound in the isonitrile reaction is interesting, as rendering it probable that the isonitriles formed by the action of chloroform and alcoholic potash on primary amines arise in a similar manner, as the former split up under the influence of mineral acids. The reason why formanilide and its homologues have not been observed in this reaction is that they are readily attacked by chloroform and alcoholic potash. Indeed, on adding these reagents to a solution of formanilide, phenyl isocyanide is at once produced; the corresponding formyl compounds of phenylhydrazine and paratolylhydrazine, however, were found to be much more stable.

In a former communication it was shown that the compound melting at  $180^{\circ}$ , which is produced along with formylphenylhydrazine, has the formula  $C_{14}H_{12}N_4$ . This was derived from analysis, from the determination of the molecular weight, and from the composition of the nitro-derivative and sulphonic acid produced from it. Its probable constitution has been expressed by the formula  $\begin{matrix} C_6H_5 \cdot NH \cdot N : C \\ C_6H_5 \cdot NH \cdot N : C \end{matrix}$ . A closer study of the behaviour of this substance led, however, to the conclusion that it is a tertiary base. The formation of a basic product from 2 mols. of the hypothetical isonitrile,  $C_6H_5 \cdot NH \cdot N : C$ , may be simply interpreted as follows:—



The two molecules condense directly to a ring in a way similar to the condensation of 2 mols. of  $\alpha$ -ketonamines or  $\alpha$ -ketonanilides in the formation of aldines, with the difference that in this latter case the condensation is accompanied by a splitting off of 2 mols. of water. A compound of the constitution given above is to be regarded as a derivative of the type  $N \begin{smallmatrix} \diagup CH \cdot NH \\ \diagdown NH \cdot CH \end{smallmatrix} N$ , a ring containing four nitrogen-atoms and two carbon-atoms, which may be called, according to Widmann's proposal (*J. pr. Chem.*, N.F., **38**, 185), *tetrazine*.

Compounds which may be regarded as derived from a nucleus consisting of four nitrogen- and two carbon-atoms are already known. These are the bodies produced by v. Pechmann (*Ber.*, **21**, 2751) by the oxidation of the osazones of 1.2 diketone compounds, and called by him *osotetrazones*. These substances are coloured, neutral compounds, easily reconverted by the action of reducing agents into the osazones from which they were formed.

Quite different, however, is the behaviour of the representative of the tetrazines produced from phenylhydrazine in the isonitrile reac-

tion, and this also confirms the view of its constitution expressed above.

*Diphenyltetrazine*,  $C_{14}H_{12}N_4$ , is dissolved with difficulty by boiling hydrochloric acid, and the solution, on cooling, deposits long, white needles of the hydrochloride, which may also be prepared by passing hydrogen chloride into an ethereal solution of the base. This salt is, however, not very stable; when boiled with water or dried at  $100^\circ$ , it splits into its components, base and acid; alcohol readily dissolves it, but, on boiling, the same decomposition seems to take place.

The analysis of the salt, dried over sulphuric acid and potassium hydroxide, gave numbers which correspond to the formula  $C_{14}H_{12}N_4, HCl$  :—

	Calculated.	Found.
Cl.....	13.027	12.74
N.....	20.55	20.90

The hydrochloride forms a double salt with platonic chloride, which may best be prepared by adding a concentrated solution of the metallic chloride to the slightly warmed solution of the base in alcohol and hydrochloric acid. After a few minutes the double salt crystallises out in yellow plates, which are washed with alcohol and dried at  $100^\circ$ .

Analysis of it led to the formula  $(C_{14}H_{12}N_4)_2, H_2PtCl_6$ .

	Calculated.	Found.			
		I.	II.	III.	IV.
Pt .....	22.055	22.21	22.11	—	—
N .....	12.70	—	—	13.18	12.91

This platinum salt is sparingly soluble in alcohol, and crystallises from it in yellow, glittering plates, which decompose about  $300^\circ$ .

The formation of a hydrochloride and of a platinochloride shows that diphenyltetrazine is a weak base, and its behaviour towards sulphuric acid characterises it as such. For the base is dissolved by boiling with dilute sulphuric acid, and, on cooling, deposits long white needles of the sulphate, which may also be prepared by adding the dilute acid to an ethereal solution of the base. The sulphate is, however, only stable in the presence of the free acid, and dissociates completely on washing with water.

Light is thrown on the nature of this base by the facts that it is indifferent towards nitrous acid and that it is not altered by boiling with acetyl chloride or with acetic anhydride, for it thus exhibits the characters of a tertiary base. The same conclusion follows also from the formation of an ammonium iodide produced by the



*Action of Methyl Iodide on Diphenyltetrazine.*

The base was heated in a sealed tube with methyl iodide in the presence of methyl alcohol for a few hours at a temperature of  $100^{\circ}$ ; the contents of the tube were then evaporated to dryness on the water-bath, and the residue boiled with water, in which it is readily soluble. On cooling, yellow needles crystallise out, which melt at  $214^{\circ}$ , and are easily soluble in alcohol. Analysis of this substance dried at  $100^{\circ}$  proved it to be an ammonium compound the *methiodide of diphenyltetrazine*.

The formula  $C_{14}H_{12}N_4,CH_3I$  requires—

	Calculated.	Found.
I .....	14.814	14.96
N .....	33.60	33.71

On adding silver chloride to a boiling aqueous solution of the iodide, silver iodide is at once formed, and the solution contains the organic ammonium chloride. On concentration, this crystallises in silky needles which melt at  $244^{\circ}$ , and are more soluble in water than the corresponding iodide.

A nitrogen determination proved it to have the formula



	Calculated.	Found.
N .....	19.55	19.72

With platinic chloride, the aqueous solution of the chloride yields a light yellow, crystalline precipitate, which is nearly insoluble in water.

The salt dried at  $100^{\circ}$  has the composition  $2(C_{14}H_{12}N_4,CH_3Cl),PtCl_4$ .

	Calculated.	Found.
Pt .....	21.376	21.35
N .....	12.31	12.57

The above described experiments afford, I think, a sufficient proof of the view that the compound formed from phenylhydrazine, in the manner stated above, is without doubt diphenyltetrazine.

The remarkable stability which this substance exhibits towards hydrochloric acid and alcoholic potash, as was mentioned in the first note (*loc. cit.*), shows itself also towards reducing agents. It may be boiled in alcoholic solutions with tin and hydrochloric acid without suffering any change; even that reducing agent, sodium and alcohol, which has so often rendered good service, has here hardly any action. By using amyl alcohol and sodium, some ammonia is, indeed, given

off, but the bulk of the substance remains unaltered. Bromine, however, acts very readily on the base, and leads to various

*Bromine-derivatives of Diphenyltetrazine.*

On adding bromine to a solution of the base in glacial acetic acid, there is at once formed a nearly white precipitate, consisting of one or more bromine substitution-products. I have repeatedly carried out this operation, but with varying results, owing to the varying quantity of bromine used and to the concentration of the solution, but I have not yet found the proper conditions for the preparation of the one or the other, as I had not the necessary quantity of material at my disposal. In one operation, using a considerable excess of bromine, a precipitate was formed consisting for the most part of *tribromodiphenyltetrazine*, as is shown by the following analyses of the product recrystallised from glacial acetic acid.

The formula  $C_{14}H_9Br_3N_4$  requires—

	Theory.	Found.
Br .....	50.74	50.40
N .....	11.84	11.97

This compound is sparingly soluble in boiling alcohol, but is readily dissolved by boiling glacial acetic acid, from which it crystallises on cooling in white needles which decompose at about  $224^\circ$ . When, however, more dilute solutions and a limited amount of bromine are used, the precipitate formed consists, for the most part, of a dibromo-derivative mixed with some of the tribromodiphenyltetrazine, as indicated by the analysis of the product recrystallised from glacial acetic acid, which gave 14.28 per cent. of nitrogen and 42.40 (42.24) per cent. of bromine, while the formula  $C_{14}H_{10}Br_2N_4$  requires 14.21 per cent. N and 40.6 per cent. Br.

Even a monobromo-derivative is produced under certain conditions by the action of bromine on acetic acid solution of the base; this was extracted from the precipitate by hot alcohol, and repeatedly crystallised from the same solvent. Its melting point was  $219-220^\circ$ , and on analysis it gave 17.70 per cent. nitrogen, whilst  $C_{14}H_{11}BrN_4$  requires 17.95 per cent. N.

A compound of the constitution 
$$\begin{array}{c} C_6H_5 \cdot N \cdot N \cdot CH \\ | \quad | \\ HC \cdot N \cdot N \cdot C_6H_5 \end{array}$$
 would give rise to three different series of bromine-derivatives, according as the substitution takes place in the phenyl-groups or in the tetrazine nucleus, or, lastly, in both at the same time. The precipitate produced by the addition of bromine to the base dissolved in acetic acid, consists

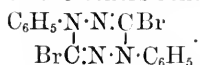
most probably of compounds which are substituted in the benzene residues of diphenyltetrazine—their melting points being above  $200^{\circ}$ .

Besides the substances above mentioned, however, another compound is produced at the same time; this is always formed by acting with bromine on the base, either in dilute or in concentrated acetic acid solution. This brominated derivative remains dissolved in the glacial acetic acid, and is thrown down by water as a brown precipitate, which is easily soluble in alcohol, and crystallises from dilute methylated spirit in faintly coloured needles which melt at  $131^{\circ}$ . Analysis proved it to be a diphenyldibromotetrazine.

Its formula  $C_{14}H_{10}Br_2N_4$  requires—

	Theory.	Found.		
		I.	II.	III.
C .....	42.64	43.00	42.48	—
H .....	2.54	3.44	3.20	—
N .....	14.21	—	—	14.33

The difference between the properties of this compound and those of the others renders it most probable that this has the constitution



The remarkable formation of a very stable compound by the action of chloroform and alcoholic potash on phenylhydrazine led me to repeat this reaction with other hydrazines, in order to determine whether they give rise to analogous compounds. I have as yet only studied the

#### *Action of Chloroform and Alcoholic Potash on Paratolylhydrazine.*

The operations were conducted in the manner described above, namely, alcoholic potash was gradually added to the solution of the hydrazine in chloroform and alcohol, the product diluted with water, shaken with ether, the unaltered base removed by means of dilute sulphuric acid, and the ethereal solution evaporated. The residue, which is an odourless oil, partially solidifies after a short time. The mass of crystals was then washed with methylated spirit and dissolved in hot alcohol, and the solution decolorised by boiling with animal charcoal; on cooling, it deposited faintly yellow plates, which melt at  $185^{\circ}$ . They are less soluble in alcohol than diphenyltetrazine, although easily soluble in glacial acetic acid.

The results of analysis, the molecular weight determinations, and the chemical behaviour, show that this compound has a constitution analogous to that of the body formed from phenylhydrazine. It is, therefore, to be regarded as *paratolyltetrazine*.

Its formula,  $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \begin{smallmatrix} \text{N} \cdot \text{CH} \\ \text{CH} \cdot \text{N} \end{smallmatrix} \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3$ , requires the following values:—

	Theory for $\text{C}_{16}\text{H}_{16}\text{N}_4$ .	Found.	
		I.	II.
C .....	72.72	72.55	—
H.....	6.06	6.70	—
N.....	21.21	—	21.24

The molecular weight of this substance was determined by Raoult's method, with the following result:—

Weight of substance.....	0.3424 gram.
„ acetic acid .....	26.2025 „
Freezing point of acetic acid ....	11.31° C.
„ of mixture .....	11.12° C.
Depression of freezing point .....	0.19° C.
Molecular weight derived from the above data .....	269
Theory for $\text{C}_{16}\text{H}_{16}\text{N}_4$ .....	264

Besides this substance there is also produced formylparatolylhydrazine, the formation of which corresponds to that observed in the case of phenylhydrazine. This compound is contained in the alcoholic filtrate from the substance  $\text{C}_{16}\text{H}_{16}\text{N}_4$ , and can be extracted by boiling water from the resin which is left behind when the filtrate is evaporated. The aqueous solution, after decolorisation, deposits white plates which melt at 164°, and on analysis proved to be formylparatolylhydrazine. The following numbers correspond to its formula,  $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{NH} \cdot \text{CHO}$ :—

	Theory for $\text{C}_8\text{H}_{10}\text{N}_2\text{O}$ .	Found.	
		I.	II.
C .....	64.00	64.10	—
H.....	6.70	7.20	—
N.....	18.67	—	18.84

This substance was also prepared by heating formamide with paratolylhydrazine in an oil-bath at a temperature of 130°, until ammonia ceased to be evolved. The resulting solid mass was recrystallised from water, when crystals were obtained which had the same melting point as the substance formed in the isonitrile reaction, and gave, on analysis, 18.80 per cent. nitrogen.

Formylparatolylhydrazine is very soluble in alcohol, sparingly in cold water, and in benzene or chloroform, and less soluble in boiling water than formylphenylhydrazine.

I am at present engaged in the further study of the two tetrazines described above, and intend also to extend the investigation of the action of chloroform and alcoholic potash to other hydrazines.

In conclusion, I may add that the formation of the formyl-derivatives of the hydrazines in this reaction led me to make some experiments with the view of producing the tetrazines from them by splitting off water, but as yet I have not been able to effect this reaction in a simple manner. I am still, however, working in this direction, and hope to be able to communicate to the Society satisfactory results.

*University Laboratory,  
Cambridge.*

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# ANNUAL GENERAL MEETING,

March 21st, 1889.

W. Crookes, F.R.S., President, in the Chair.

The pleasant duty again devolves on me to present to you the annual report on the state of the Chemical Society during the twelve months just past.

The following tabular statement shows the numerical position of the Society :—

Number of Fellows (March 28th, 1888).....	1534	
Since elected and paid admission fees.....	140	
		<hr/>
		1674
Deceased.....	23	
Withdrawn.....	16	
Removed on account of arrears .....	21	
	<hr/>	60
Present number of Fellows .....	1614	
Increase .....	80	
Number of Foreign Members .....	37	
Deceased (Professor H. Debray).....	1	
	<hr/>	
Present number of Foreign Members.....	36	

Our losses from death include several well-known names. They are on the home list :—Professor Brazier, John Collins, R. Cartmell, J. J. Coleman, W. F. Donkin, H. C. Foote, Peter Griess, A. N. Gow, John Horsley, J. M. Kavanagh, J. D. Perrins, Dr. David Price, F. G. Ree, J. Robinson, W. O. Senier, J. Denham Smith, J. Storey, James Taylor, J. S. Topham, Thomas Ward, Dr. W. Wallace, G. J. Wishart, John Williams. And one Foreign Member, Professor H. Debray.

Withdrawn :—R. Byramjee, C. B. Caswell, Dr. E. A. Cook, R. Coulthard, P. N. Datta, Charles E. Ellis, F. A. Genth, Jun., C. H. Gimingham, Andrew Henderson, Edward Hunter, W. J. Noble, Walter Pearce, Dr. B. W. Richardson, J. P. Smith, Ed. S. Spalding, and Oswald Wilkinson.

Removals on account of non-payment of subscriptions:—J. B. Bardslèy, William Bedford, R. G. Blaine, Professor A. C. Dixon, A. E. Drinkwater, U. K. Dutt, Rev. W. H. Eley, E. H. Farmer, W. F. Fremersdorff, F. G. Holmes, J. J. Knight, J. L. Muspratt, Robert Marr, S. R. Pontifex, Thomas Perry, R. H. Ridout, G. H. Rutter, W. Robinson, Franz Rindskopf, F. M. Sexton, and J. W. Stevens.

In the year 1888, there were 75 original papers published in the Journal, occupying 895 pages, as compared with 88 papers of 871 pages in 1887. The Abstracts in 1888 occupy 1351 pages, compared with 1159 in 1887. The number of Abstracts is 2470 compared with 2277 in 1887.

103 papers have been communicated to the Society this session. Several of these papers were published in full in the Proceedings, and Abstracts of all have also there been given.

The Proceedings of the Chemical Society, appearing as it does soon after each evening meeting, is valuable as affording country members a rapid and trustworthy account of what goes on at our Society, and has now taken a well established position as an independent publication.

Our Library continues to increase, and every year becomes richer in rare volumes and books of reference. The duplicate library for lending is also becoming increasingly useful. The following table shows the present state of our shelves:—

	March 31st, 1888.	Addition in 1888-89.	Present State.
Volumes of systematic works.....	2,780	142	2,922
Volumes of journals.....	5,119	355*	5,474
Volumes of duplicate journals for circulation.	941	143†	1,084
Pamphlets.....	1,410	16	1,426
	10,250	656	10,906

The expenditure under this head for the current year is £308 5s. 6d.

The following table shows the position of the Journal during the past year, as compared with the previous four years:—

\* Including 170 vols. *Dingler's Polytechnisches Journal*.

† Including 95 vols. *Dingler's Polytechnisches Journal*.

	1884.	1885.	1886.	1887.	1888.
General and Physical Chemistry..	237	331	235	271	340
Inorganic Chemistry.....	189	191	223	242	216
Mineralogical Chemistry .....	192	201	223	180	171
Organic Chemistry .....	939	1047	1056	1045	1088
Physiological Chemistry.....	118	142	100	100	153
Chemistry of Vegetable Physio- logy and Agriculture.....	324	218	160	123	170
Analytical Chemistry .....	256	337	289	316	332
Technical Chemistry.....	286	280	66*	—	—
Total.....	2541	2747	2352	2277	2470
Papers in Transactions.....	57.	85.	85.	88.	75.

I must now ask your attention to an event of which none of you can be ignorant, which, though not exclusively relating to chemistry, bears closely upon it and upon the future of British science. I refer to the protest against the examination system in education which appeared in November last. That protest had long been in the air. For years past men who take the trouble to observe and to reflect have come to the conclusion that competitive examination is injurious to the individual, injurious to the race, and that it starves original research at the very root. They have convinced themselves that if we flag in scientific investigation, that if a large and increasing proportion of professorships and of leading positions in industrial establishments, both in the home kingdom and in the colonies, are filled by aliens, the fault lies mainly with our educational system. Men trained chiefly to pass examinations either in theoretical or practical departments cannot equal those who have been schooled in actual research, trained to accurately observe and draw correct inferences from facts. All the earlier protests were desultory, and calculated to produce no lasting impression; but the recent manifesto is the expression of the collective opinion of many earnest representative men and women. Hence it cannot be slighted as the mere outcry of a faction, a sect, a school, or an interest.

A most satisfactory feature is the adhesion to the protest of men who formerly were in favour of competitive examination as the test for entrance into the civil or military service of the State. Professor Max Müller, of Oxford, frankly admits he now considers competition to be a mistake, and avers that the failure springs not only from the manner in which the system has been worked, but is involved in its very nature. But if this protest is to avail it must be energetically

\* The Technical Division was discontinued after the April number, 1886.



followed up, for I must repeat what I have before declared, that the position of science in Britain is far from satisfactory.

Though the number of articles devoted to research in German transactions and journals exceeds those in our own publications, we must remember that the population of the German Empire is greater than that of the United Kingdom by at least one-fourth; further, that the *savants* of Russia, of the Austrian Empire, of Switzerland, of Holland, and Scandinavia largely select German journals as their medium of publication. Not a few English and American scientific men follow the same course. Hence, as regards quantity, our share in the world's scientific work is more considerable than appears at the first glance. Further, I think that if deficient in quantity English research excels in quality. If we do less detailed work we furnish a larger proportion of generalisations and laws than most of our rivals. As the discoverers of laws and generalisations, Black, Boyle, Dalton, Faraday, Graham, Joule, Newton, Wollaston, and Young are household words in the laboratory—yet none of these men were the products of the examination system.

There is another evil against which I must strongly protest. I refer to the system of “sealed papers.” Everyone knows that on the Continent, more especially in France, it is common for anyone who has, as he thinks, approached the solution of some important question, to deposit a sealed sketch of his incomplete results with the President or Secretary of some learned society. The sketch may lie *perdu* for years, until the author requests it may be opened and read before the Society. The practice arose from a desire that the author's priority should be guaranteed against others who might lay claim to his ideas. But priority can be quite as effectually secured by a brief preliminary notice read before some Society or sent to some journal, the author thus reserving to himself the further investigation of the subject. Among men of honour such reservations are invariably respected. But the “sealed paper” system lends itself to something which borders unpleasantly upon fraud.

Suppose an investigator takes up some question, sees that it admits of two or more solutions, or that various hypotheses present themselves to him as possible. To work out the matter conclusively might require much time and trouble. He therefore writes out each hypothesis, and incloses them separately in “sealed papers” duly numbered, carefully retaining copies. In process of time, some other investigator, ignorant of what the first author has done, takes up the subject and works out one of these hypotheses to demonstration. So soon as his supplementary memoir is before the world, the first investigator requests that the “sealed paper” No. 2 or No. 3 be opened and read. The new theory, laboriously considered and worked out,

is found to have been anticipated, and the man who has really done the work is robbed of much of his credit. The seeming anticipator says nothing about the contents of other "sealed papers," in which he has proposed totally different hypotheses; these he now leaves to oblivion.

I think the Fellows of our Society will agree with me that a system which thus enables a man to reap the fruit of another man's experiments does not deserve to be naturalised in England.

There is a further abuse to which attention may usefully be drawn. It sometimes happens that a man of science will send an account of researches he has completed to two journals simultaneously, English or foreign, leaving each editor under the impression that he is the sole recipient of the communication. Or, still worse, a man reads a paper before our Society and sends it to some foreign journal, so that it may figure in print before it appears in the Society's Transactions.

To this subject I felt compelled to refer when I had the honour of addressing you last year. And you are now aware, your Council has resolved that no memoir be published which has previously appeared in a foreign journal unless specially recommended by the Publication Committee and approved by the Council. The reasons for this resolution are not hard to seek. Not merely is the reputation of the Society, as the original channel of the researches in question, imperilled, or at least obscured, but a serious waste of time and labour is inflicted upon anyone who needs to read up the literature of the subject. We, in England, are by no means the only sinners in this respect. It often happens that memoirs which have been read before the Paris Academy of Sciences reappear as "original matter" in certain French journals.

I cannot pass over a discovery made this season by Dr. Krüss concerning nickel and cobalt. As at first reported, it seemed that these two metals might be eliminated from our text-books, and that two or three new substances would take their place. Had this been the case it would undoubtedly have been one of the greatest steps in pure chemistry taken this century. It now appears that each of the two metals contains a common impurity which Dr. Krüss has been the first to detect and isolate. Nickel and cobalt thus purified will still retain their individuality, though their accepted properties, physical and chemical, will need careful revision.

In any case the discovery is most instructive, warning us how careful we should be to have firm ground under our feet. It is almost humiliating that two metals which have been subjected to infinite research and scrutiny, should now be found to contain such a proportion of unsuspected impurity.

You are aware that at the ballots for the election of Fellows half

an hour or more of valuable time is thus spent in a manner which, to say the least, is not very interesting. An attempt has been made to save time by taking the ballot in the library, after the meeting, but so many Fellows leave before the end of the meeting that the number remaining has not been found sufficient to meet the requirement of the bye-laws. Your Council have from time to time had this matter under discussion, and at their last meeting, on the 21st inst., it was resolved "That in future the balloting for Fellows be conducted by means of papers." The best manner of carrying out this resolution will be a subject for future arrangement.

A posthumous memoir on the compressibility of hydrogen, by the late Professor Wroblewski, reminds us of the sad and untimely death of this meritorious and distinguished worker in physical chemistry. His death, as most of us doubtless are aware, was due to the frightful burns which he received from the overturning or explosion of a paraffin lamp. In the memoir in question, Professor Wroblewski treats of the compressibility of hydrogen at  $99^{\circ}$ , at  $0^{\circ}$ , at  $-103.5^{\circ}$  (boiling point of ethylene), and at  $-182.4^{\circ}$  (boiling point of oxygen), for pressures ranging from 1 to 70 atmospheres. From the results, the following data were calculated:—Critical temperature,  $-240^{\circ}$ ; critical pressure, 13.3 atmospheres; critical volume, 0.00335. Hence it appears very doubtful whether M. Pictet or M. Cailletet really succeeded in liquefying hydrogen.

Last year I had the pleasure to announce that one of our Fellows, Mr. Newlands, had received the "Davy Medal" of the Royal Society for his splendid discovery of the Periodic Law of the Chemical Elements. I may also be allowed to state that to me, your President, the Royal Society has likewise awarded the same distinction for my Researches on the Behaviour of Substances under the influence of the Electric Discharge in a High Vacuum, with especial reference to their Spectroscopic Reactions.

Hence it has been suggested that I might not unprofitably claim your attention this evening for a history of the so-called rare earths, as they have been brought to light and discriminated by the aid of the spectroscope.

If I name the spectroscope as the most important scientific invention of the latter half of this century, I shall not fear to be accused of exaggeration. Photography has rendered vast services in recording astronomical and biological phenomena, and it even supplies us with indirect means of studying ray vibrations to which the human retina does not respond. The electro-acoustic devices of Edison and his co-workers permit almost magical communication between human beings. Ruhmkorff's coil and the Geissler tube have rendered notable service in physical investigation; and the electric lamp

promises to aid in exploring the internal parts of living animals as well as in studying the organic forms of the deep sea. But in the spectroscope we possess a power that enables us to peer into the very heart of Nature. In the extent of its grasp and the varied character of its applicability it surpasses the telescope, and at least rivals the microscope. It enables the astronomer to defy immeasurable distance, and to study the physical condition and the chemical composition of the sun and the stars as if they were within touch, and even to ascertain the direction of their movements.

Without attempting to discuss the import of the results thus gained—which would lead us too far—I may point out that they overthrow a dogma concerning the classification of the sciences. It has been said that the simpler and more general sciences lend both doctrines and methods to the more complex and less general sciences, and that the latter give nothing in return. But we now see chemistry endowing astronomy with an original and fruitful method of research.

Turning to the very opposite extremity of the scientific hierarchy we find that to the biologist the spectroscope is of value in studying the relations of animal and vegetable fluids, and even of certain tissues. But this wonderful instrument is clearly destined to play its chief part in what is called terrestrial chemistry—the field where it has won the most signal triumphs.

It must be remarked, despite this vast range of applicability, a range sweeping through the whole universe and embracing all the four elements of antiquity; and despite the astonishing results already achieved and the prospect of greater revelations to come, that the spectroscope is still inadequately appreciated by professed men of science, and in consequence is to a great extent ignored by the “educated and intelligent public.” In urging its more thorough recognition I do not advocate the formation of spectroscopic societies for the fragmentary study of everything that can be observed with a spectroscope. But I recommend researching chemists to appeal to this instrument wherever requisite and possible.

An elaborate spectroscopic study of the basic constituents of rare minerals from different localities would be of great value, and I would suggest that on all possible occasions meteorites should be submitted to careful spectroscopic analysis.

I do not propose to discuss all the splendid achievements of the spectroscope in chemistry; nor its applications in ordinary analysis, qualitative and quantitative; nor the conduct of technical operations, such as the Bessemer process. I confine myself to the light thrown by the spectroscope upon the nature and the relations of our *elements*, real or supposed.

Though systematically employed by few experimentalists, the spectroscope has already led to the discovery of several hitherto unknown elements. In the early days of spectrum analysis attention was mainly concentrated on the flame spectra: that is, the bodies in question were vaporised and rendered luminous by the action of a flame, such as that of the Bunsen burner or of the oxyhydrogen jet. This procedure in the hands of Bunsen and Kirchhoff gave us cesium and rubidium; afterwards in my own hands, thallium; and in those of Reich and Richter, indium.

Then followed the production and examination of spark-spectra. The spark produced by means of the induction coil, especially when its energy is reinforced by the intercalation of a Leyden jar, volatilises and renders luminous minute portions of matter, solid, liquid, or gaseous, which may then be examined by the spectroscope. In this manner gallium was discovered in 1875 by Lecoq de Boisbaudran. In consequence of the sharpness and the well-marked character of these spark-spectra they are relied on by chemists as certain proof of the identity of any two elements which yield identical spectra.

Next was introduced the systematic study of the absorption-spectra seen when a beam of light is passed through certain transparent solids or through solutions of various substances. One of the earliest observers in this branch of spectroscopy was Dr. Gladstone, who, in 1858, read before this Society a paper on the absorption of light by various metallic salts, and gave the first description of the absorption-spectrum of didymium. This branch of spectroscopy has proved not less fruitful in the recognition of new metallic elements.

In the investigation of the rare earths my principal object has been to separate the true from the undemonstrated and spurious, verifying the true, rejecting the spurious, and reducing as far as possible the number of the doubtful. In the following table I have given a list of the so-called "rare elements," with which for the last seven or eight years I have been specially occupied. Column 1 gives the names by which they are commonly known. Column 2 gives their atomic weights, &c. Column 3 shows in what manner they come under the domain of spectroscopy; and columns 4 and 5 notify the components or meta-elements into which some of these bodies have been decomposed in 1886 by myself, and in 1887 by Krüss and Nilson. In the first column I have exercised a judicial leniency in retaining candidates, for the sake possibly of old associations, when strict justice would have disestablished them. Thus, it may be doubted whether decipium, philippium, or gadolinium should have been retained. But since doubts have been cast on the integrity of nearly all the occupants of this column the line should not be drawn too strictly.

TABLE I.

	Atomic weight of metal and formula of oxide.	Gives spectrum by—	Component meta-elements according to—	
			Crookes (1886).	Nilson and Krüss (1887).
Didymium . . . . .	$\left\{ \begin{array}{l} \text{Neodymium—} \\ 140.3. \text{Nd}_2\text{O}_3. \\ \text{Praseodymium—} \\ 143.6. \text{Pr}_2\text{O}_3. \\ \text{Unnamed.} \end{array} \right\}$	Absorption.	$\left\{ \begin{array}{l} \text{Da} \\ \lambda = 475 \end{array} \right\}$	$\left\{ \begin{array}{l} \text{Dia} \\ \text{Di}\beta \\ \text{Di}\gamma \\ \text{Di}\delta \\ \text{Di}\epsilon \\ \text{Di}\eta \\ \text{Di}\theta \\ \text{Di}\iota \\ \text{Di}\kappa \end{array} \right\}$
Decipium . . . . .				
Samarium . . . . .	150.12. $\text{Sm}_2\text{O}_3$ .	Absorption and phosphorescence.	$\left\{ \begin{array}{l} \text{S}\delta \\ \text{G}\epsilon \\ \text{G}\gamma \\ \text{G}\theta \end{array} \right\}$	$\left\{ \begin{array}{l} \text{Sma} \\ \text{Sm}\beta \end{array} \right\}$
Lanthanum . . . . .	138. $\text{La}_2\text{O}_3$ .	Phosphorescence.		
Erbium . . . . .	166. $\text{Er}_2\text{O}_3$ .	Absorption and phosphorescence.	$\left\{ \begin{array}{l} \lambda 550 \\ \lambda 493 \end{array} \right\}$	$\left\{ \begin{array}{l} \text{Era} \\ \text{Er}\beta \end{array} \right\}$
Philippium . . . . .	45—48. $\text{PpO}$ .	Phosphorescence.		
Holmium . . . . .	—	Absorption.	—	$\left\{ \begin{array}{l} \text{Xa} \\ \text{X}\beta \\ \text{X}\gamma \\ \text{X}\delta \end{array} \right\}$
Thulium . . . . .	170.7. $\text{Tm}_2\text{O}_3$ .	Absorption.		$\left\{ \begin{array}{l} \text{Tma} \\ \text{Tm}\beta \end{array} \right\}$
Dysprosium . . . . .	—	Absorption.	$\lambda 457\text{—}448$ (1888)	$\left\{ \begin{array}{l} \text{X}\zeta \\ \text{X}\epsilon \\ \text{X}\eta \end{array} \right\}$
				Lecoq de Boisbaudran.
Yttrium . . . . .	88.9. $\text{Yt}_2\text{O}_3$ .	Phosphorescence.	$\left\{ \begin{array}{l} \text{Ga} \\ \text{G}\beta \\ \text{G}\delta \\ \text{G}\zeta \\ \text{G}\eta \end{array} \right\}$	$\left\{ \begin{array}{l} \text{Za} \\ \text{Tb} \\ \text{Yt} \end{array} \right\}$
Terbium . . . . .	124.7. $\text{Tb}_2\text{O}_3$ .			
Gadolinium (Ya)	—	Phosphorescence.	$\left\{ \begin{array}{l} \text{G}\beta \\ \text{G}\zeta \end{array} \right\}$	
Ytterbium . . . . .	173.01. $\text{Yb}_2\text{O}_3$ .	Phosphorescence.		
Scandium . . . . .	44.03. $\text{Sc}_2\text{O}_3$ .			

At first spectroscopic examination was applied directly to substances, natural or artificial, which had not undergone any special preparation. The idea next occurred of attempting to split up substances supposed to be simple into heterogeneous constituents before appealing to the spectroscope. The refined chemical processes used for this operation may be summarised under the name of fractionation, whether they be fractional precipitations, crystallisations, or decompositions. The essential principles of this process were so

fully discussed on the last occasion when I had the honour of addressing you that I need not further allude to them.

### *The Didymium Group.*

A combination of such delicate and prolonged chemical processes with spectroscopic examination applied to bodies showing absorption spectra soon led to important discoveries. Fig. 1A\* shows what I may call the normal didymium spectrum, as it was generally recognised down to the year 1878. Fig. 1B shows the whole of the absorption-bands belonging to bodies subsequently separated from didymium by fractionation. When in 1878 the didymium from samarskite was examined by Delafontaine (*Compt. rend.*, **87**, 632; *Chem. News*, **38**, 223) he found it to differ somewhat from ordinary didymium as extracted from cerite and gadolinite, and by a series of chemical fractionations he succeeded in separating from it an earth which he called decipium, giving at least three absorption-bands, one having a wave-length of 416 ( $1/\lambda^2$  578); another narrower and stronger, at wave-length 478 ( $1/\lambda^2$  438), and a very faint "minimum of transmission" near the limit of the blue and green. Nine months later Lecoq de Boisbandran (*Compt. rend.*, **89**, 212; *Chem. News*, **40**, 99) announced the discovery of samarium as a constituent of the didymium from samarskite, giving a drawing of the decipium and samarium spectra to a common scale (Fig. 2), from which it is seen that samarium is characterised by the bands of Delafontaine's decipium together with two additional bands. Fig. 3 shows the samarium spectrum from the latest measurements.

Still didymium was not reduced to its ultimate simplicity. In 1885 Carl Auer (*Monatsh. Chem.*, **6**, 477), by fractionally crystallising the mixed nitrates of ammonium, didymium, and lanthanum, showed it was thus possible to cleave didymium in a certain direction and separate it into two other bodies, one giving green salts and the other pink salts. Each of these has a characteristic absorption-spectrum, the sum of the two sets of bands approximating to the old didymium spectrum. These bodies the discoverer has named respectively praseodymium and neodymium. The neodymium spectrum (Fig. 4), according to Auer, consists of the whole of the bands in the red, with part of the large one in the yellow; it then misses all the green and blue, and takes in the second line in the violet. Fig. 5 is the spectrum of praseodymium, which I have also taken from Auer's description; it takes the other part of the yellow band and all the green and blue, except the second blue, which belongs to neodymium. Subtracting these two spectra from the old didymium

\* All the figures are drawn to the  $1/\lambda^2$  scale.

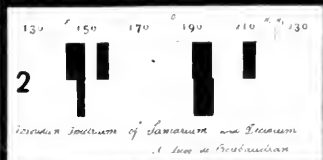
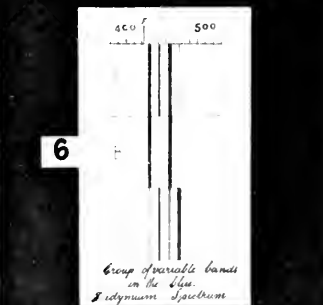
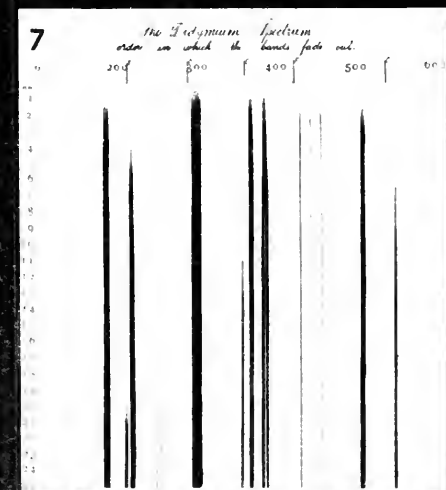
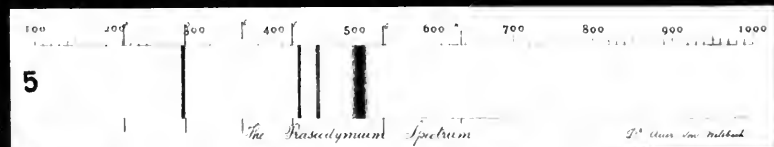
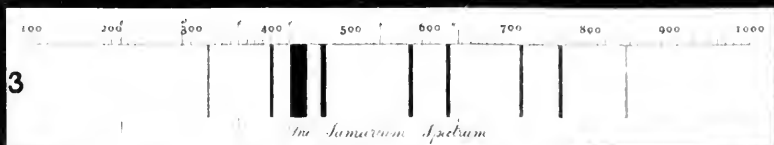
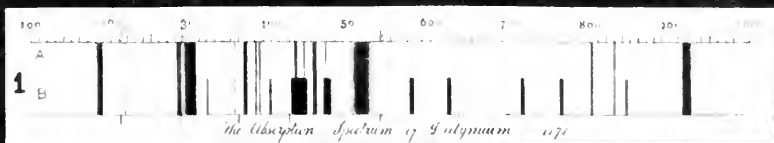
spectrum (Fig. 1) you see there are still two bands left at  $\lambda$  462 and 475 ( $1/\lambda^2$  465 and 443). Assuming that the argument from absorption-spectra is a legitimate one—and all recent research tends to show that if not quite trustworthy it is at all events a weighty one—the inference I draw from these results is that the old didymium still contains a third body distinct from neo- and praseo-dymium, to which one or both of these extra bands is due.

I must venture to lay especial emphasis on the words *in a certain direction*. Didymium in my own laboratory has undergone other cleavages, and I have not yet decided whether we shall have to recognise further decompositions of neo-dymium and praseo-dymium, or whether the original didymium is capable of being resolved differently according to the manner in which it is treated. Keeping the band in the orange always of the same strength, in many of the fractions of didymium from different sources the other bands of neo- and praseo-dymium are seen to vary from very strong almost to obliteration (*Chem. News*, 54, 27). In this way I have worked on the spectra of didymium from allanite, cerite, euxenite, fluocerite, gadolinite, hielmite, samarskite, yttrotitanite, &c., and the further I carry the examination the more the conclusion is forced upon me that didymium must not be regarded as compounded of two elements only, but rather as an aggregation of many closely allied bodies. Later researches of Krüss and Nilson have led them to the same conclusion.

When working in 1886 on the decomposition of the nitrate of didymium by heat, I found very decided indications of the possibility of depriving didymium of band after band until only the deep line in the blue  $\lambda$  443 ( $1/\lambda^2$  509.6) is left (*Proc. Roy. Soc.*, 40, 503). I have provisionally named this single band element Da. In this connection I would like to draw your attention to a few facts which have very recently come to light.

In some of my fractions of didymium the band  $\lambda$  475 ( $1/\lambda^2$  443) intensifies in company with another band at  $\lambda$  462 ( $1/\lambda^2$  465). Fig. 6 shows at A the group of blue bands as they are seen in a strong solution of didymium. It forms a well-marked set of four comparatively sharp lines, one at  $\lambda$  462 ( $1/\lambda^2$  465) being the faintest. Under these lines I show (Fig. 6, B) the same group as seen in fractions of the same solution of didymium after disintegration has commenced. This fraction is very similar to Auer's praseo-dymium; and below this (Fig. 6, C) I again show the same group as seen in the didymium fractions most removed from the one last described. Here the two lines  $\lambda$  475 ( $1/\lambda^2$  443) and  $\lambda$  462 ( $1/\lambda^2$  465) have become very strong, while the other two have almost faded out. One of these,  $\lambda$  475 ( $1/\lambda^2$  443), is included by Auer in the spectrum of his crude didymium, but he makes no further reference







to it either in description or diagram. Of these lines,  $\lambda$  462 ( $1/\lambda^2$  645), probably belongs to the samarium group, but the other,  $\lambda$  475 ( $1/\lambda^2$  453), cannot belong to samarium, although it superposes on the most refrangible half of the broad and ill-defined samarium band.

In a paper read before the Royal Society dated June 9, 1886 (*Compt. rend.*, **102**, 1551), I gave an account of some observations I had made upon the line  $\lambda$  475 ( $1/\lambda^2$  443), proving that it could be separated from the old didymium spectrum, and in conclusion said it "must be regarded as characteristic of a new body."

Subsequent to my paper Demarcay (*ibid.*) drew attention to this line at  $\lambda$  475 ( $1/\lambda^2$  443), and in 1887 (*Compt. rend.*, **104**, 580) he again returned to the subject, associating the two lines  $\lambda$  475 ( $1/\lambda^2$  443) and  $\lambda$  462 ( $1/\lambda^2$  465) as being due to the same element. With this opinion I cannot yet agree, for in many instances I have had fractions in which the relative intensities of the two are widely different. More recently Krüss and Nilson have ascribed this line to one of the constituents of Soret's X or holmium, which gives a line falling nearly on the same place (*Chem. News*, **56**, 154, 173).

By examining the absorption-spectra of solutions of rare earths obtained from widely different sources, Krüss and Nilson (*Ber.*, **20**, Part XII, 2134; and *Chem. News*, **56**, 74, 85, 135, 145, 154, 165, 172) came to the conclusion that the elements giving absorption-spectra, and known as didymium, samarium, holmium, thulium, erbium, and dysprosium, were not homogeneous, but that each one contained almost as many separate components as it produced bands of absorption.

They have discovered that in didymium obtained from some minerals one of the fainter lines of the normal didymium spectrum is strong, while others usually stronger are almost or quite absent; results to which I shall presently refer will show that this cannot be explained by dilution or concentration. In this way, by examining a great number of minerals, they found anomalies occurred in the case of almost each of the old didymium lines, and therefore decided, as above mentioned, that it is a compound body, capable of resolution into at least nine separate components.

Identical arguments are brought forward to prove that each of the other so-called elements, samarium, erbium, holmium, thulium, dysprosium, &c., are compounds of many closely allied bodies.

Krüss and Nilson, I believe, are pushing their investigations with the object of isolating the separate components of these different earths. They, however, question the possibility of resolving the erbia and didymia earths into their several ultimate constituents by a fractionated decomposition of the nitrates. In fact they assert that

by means of the methods of separation at present known it would be almost impossible to completely isolate any single constituent of the mixed earths. They therefore propose, as I had previously done,\* a method by which we may certainly arrive nearer to the mark and dispense with much tedious fractionation. If we examine the minerals which contain these rare earths we find they occur in very different states of mixture or combination. Sometimes many of the constituents which we wish to separate are conjointly present, and sometimes but few. The desired differentiation, in fact, has already been commenced by Nature. Krüss and Nilson, therefore, whichever ingredient they wish to separate, propose to operate on a mineral which contains that ingredient as far as possible in a state of isolation. In other words, they will take advantage of the work that Nature has already begun, and endeavour by refined chemical means to put the last finishing touches to her work. Thus they will be able to work with smaller quantities of primary material,—no small consideration in the case of some minerals,—and to obtain results in a shorter time. How widely the composition of one and the same mineral, as judged by our searching physical tests, may vary, will be seen from the following instances. Fergusonite from Arendal shows six of the bands of holmium, fergusonite from Ytterby four, and that from Hitterö only three. Moreover, the ingredient provisionally called X<sub>2</sub> is to be found in the fergusonite from Ytterby, but not in that of Arendal and Hitterö.

The foundation for thus firmly declaring what I had previously ventured to infer, is the striking differences in the spectra given by several specimens of one earth, say didymium, when obtained from different sources.

We are anxiously waiting the results of this investigation, but although the paper quoted was published in July, 1887, no further communication has come from these illustrious workers.

Chemists recently have stated as proof of the existence of new elements the fact that certain bands of absorption, as seen in various fractions, "follow the same variations of intensity." Before deciding the question whether didymium is a homogeneous whole, or whether an argument in favour of its heterogeneity can be based on the fact that the absorption-spectra of didymium from different minerals differ *inter se*, it was necessary to ascertain if the absorption-bands seen in its solutions, whatever the thickness of the layer, whether dilute or concentrated, followed the same variations, and also to ascertain the nature of these variations. To contribute to this

\* "Address to the Chemical Section of the British Association, Birmingham Meeting," *Chem. News*, 54, 123. "On the Fractionation of Yttria," *Chem. News*, 54, 157. *Proc. Roy. Soc.*, 40, 1886, 5 5.

inquiry I examined the absorption-spectrum of a solution of neutral didymium nitrate containing one part by weight of metal in 10 of water, as seen through a series of cells from 1 mm. to 25 mm. in thickness. For this work I used a new form of binocular spectroscope, fitted with a mechanical tracing arrangement, so that each spectrum can be automatically mapped on paper strips; from this set of tracings I have arranged the diagram (Fig. 7) now before you. It represents the bands of the normal didymium spectrum. The figures running up the side represent the thickness of the layer of solution observed, and they show at a glance the "life" of each of the bands. At the bottom, 25 mm. thickness, all the known bands are visible, and they become fainter and die out in the particular order here given, some of them remaining visible almost to the end. For instance, almost as long as the deep line in the blue part of the spectrum at  $\lambda$  443 ( $1/\lambda^2$  509), my D $\alpha$ , can be distinguished, it is possible to see the group of three very narrow ones next to it. Two or three other less characteristic bands can be seen only when there is a very considerable depth of liquid; thus, the three lines in the red  $\lambda$  636, 628, 622 ( $1/\lambda^2$  247, 253, 258), cannot be seen distinctly through less than 20 mm. of this strength of solution.

Having ascertained in this series how the spectra varied in appearance with different thicknesses of the same solution (strength 1 of Di in 10 of water), I repeated the experiments, keeping the thickness of layer of solution constant, and diluting the standard solution of didymium so that the rays of light passed through the same quantity of metal as in the former series. The results in each case were practically identical; the differences being too slight to be detected in my apparatus. The spectrum exhibited, for instance, by 1 mm. of the standard solution of didymium is found to be identical with the spectrum shown by the same solution diluted 20 times and viewed through a 20 mm. cell.

It will be seen that in the case of 1 mm., not only the line in the yellow at  $\lambda$  582 ( $1/\lambda^2$  292)\* is to be seen, but also two in the green at  $\lambda$  525 ( $1/\lambda^2$  368) and  $\lambda$  510 ( $1/\lambda^2$  382). Therefore, to get a more simple spectrum, I diluted the solution to 1 of didymium in 20 of liquid. 1 mm. thickness of this shows little else than a broad faint trace of the line in the yellow,  $\lambda$  582 ( $1/\lambda^2$  292).

In the year 1886 (*Proc. Roy. Soc.*, **40**, 502, June 9, 1886; *Chem. News*, **54**, 27, July 19, 1886) I demonstrated from experiments on the fractionation of didymium that this element was very probably a compound capable of being resolved into a number of constituents, each represented by a single band, like the cases of yttrium and

\* The  $\lambda$  and  $1/\lambda^2$  lengths given here are only approximate.

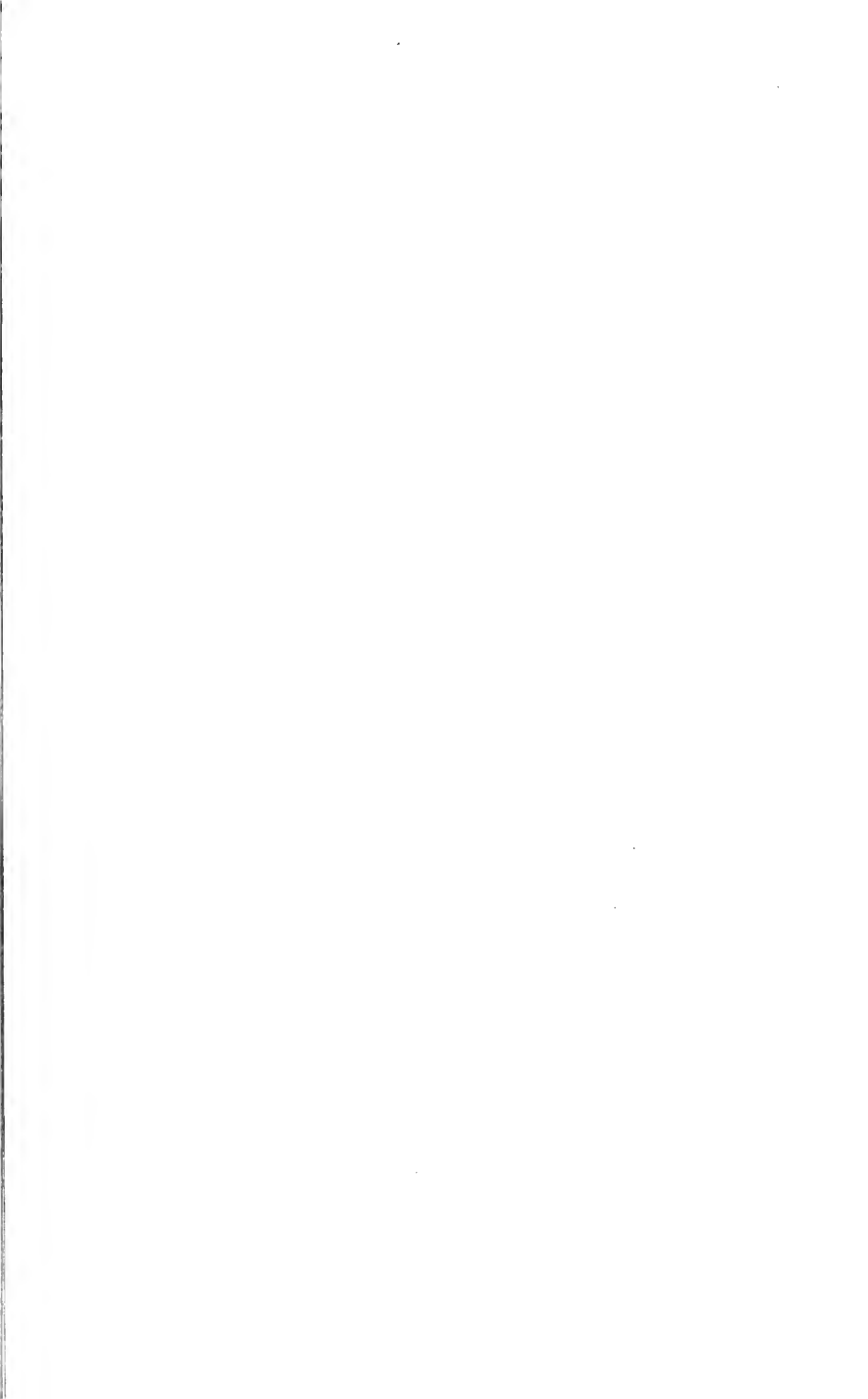
samarium, which give bands by phosphorescence. In Krüss and Nilson's case, the batch of crude earth contained in any single mineral was examined as a whole without any attempt to separate the earths, and the composition of some of these minerals is extraordinarily complex, euxenite for example containing, after removal of the other metals, the rare bodies Ce, La, Di, Sm, Yt, Er, Tr, Ho, Tm, Th, De, Sc, Dy, Be, Nb, Ta.

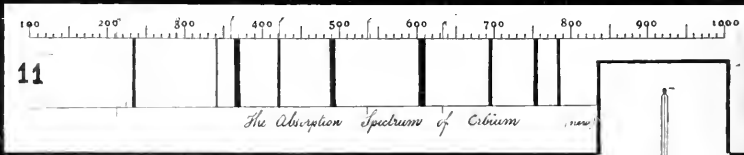
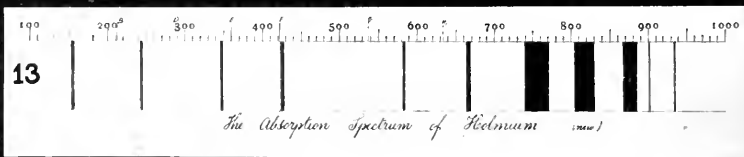
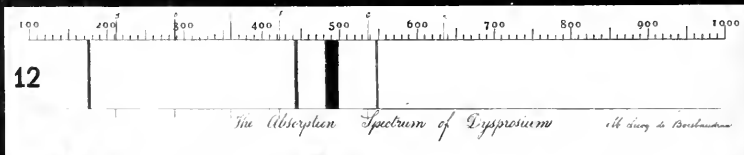
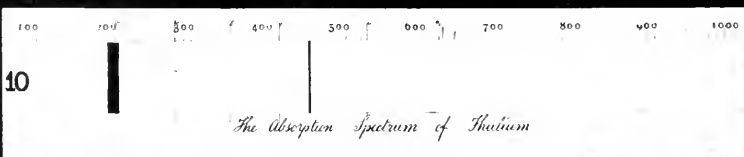
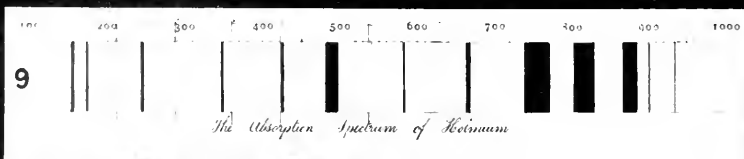
In my own case the didymium earths, upon which I formed the "one band one element" theory (*Chem. News*, 54, 27) were in a much more simple state, as the whole of the yttrium group, including erbium, holmium, thulium, &c., and others, had been removed, and the earth under examination probably contained little besides didymium and lanthanum, with traces only of samarium, yttrium, and calcium. But not even here was the earth under examination in a state of even approximate purity.

There are at least two points in these researches that I must touch, since they illustrate the necessity of great caution in drawing conclusions from an examination of absorption-spectra. Paul Kiewewetter and Krüss (*Ber.*, 21, 2310; *Chem. News*, 58, 75, 91) have recently published a paper on this subject, although it goes no further, nor indeed so far as the previous communication of Krüss and Nilson. They have examined gadolinite, and find that some constituents of didymium and samarium are absent, notably those which produce the group of lines in the green to which I have already referred. In my own laboratory I have worked for the last two years almost exclusively upon the earths from gadolinite—of which I have obtained a large quantity from Fahlun—and there is not the shadow of a doubt that in my gadolinite earths the lines reported absent by Kiewewetter and Krüss are present in abundance.

Some hitherto unexplained condition doubtless rendered these lines invisible to Kiewewetter and Krüss; perhaps the presence of some other earths, or some condition of concentration or acidity. In the light of this knowledge I do not see how we can take the results of Krüss and Nilson or my own as final.

Concerning the influence of one body upon another little is yet known, but that little is of sufficient importance to make us very careful how we interpret absorption-spectra when uncorroborated by chemical results. Lecoq de Boisbaudran and Smith have pointed out some important modifications produced in absorption-spectra by an excess of acid (*Compt. rend.*, 88, 1167), and later on Soret (*Compt. rend.*, September 15, 1879) verified these observations. Brauner and others have recorded experiments on mixing solutions of didymium and samarium; they find, in the case of a didymium solution showing the group of three bands,  $\lambda$  476, 469, 428 ( $1/\lambda^2$  430.4,

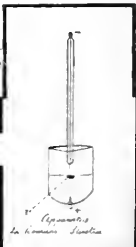




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441·3, 454·6), that by adding a dilute solution of samarium, all three of these bands vanish without any appearance of any of the samarium bands, until a certain proportion is reached, when the samarium bands gradually come in their place (Brauner, *Trans. Chem. Soc.*, 1883, **43**, 286). In my own experiments, I find that from a solution of erbia which originally shows no trace of the strong didymium band lying between  $\lambda$  596 and 572 ( $1/\lambda^2$  281 and 305), appreciable quantities of didymium can certainly be squeezed out by fractionation.

Owing to its complicated nature, Kiewewetter and Krüss consider gadolinite an unfavourable source of didymium for these investigations, and recommend that a large quantity of earth from keilhanite should be systematically worked up, for the reason that keilhanite didymium is more simple in constitution.

### *The Erbium Group.*

It is known that a certain oxide, 10 years ago called erbia, and regarded as belonging to a simple elementary body, has been resolved by the investigations of Delafontaine, Marignac, Soret, Nilson, Clève, Brauner, and others into at least six distinct earths—three of them, scandia, ytterbia, and terbia, giving no absorption-spectra, whilst others, erbia (new), holmia, and thulia, give absorption-spectra.

In Fig. 8A I have represented the old erbium absorption-spectrum, as it was known down to the year 1878. In Fig. 8B, as in the case of didymium, I have given for diagrammatic purposes certain lines which, not seen in unfractionated erbia, belong to bodies capable of being separated from it by fractionation.

The first to announce that erbium was not a simple body was Delafontaine, who in 1878 (*Compt. rend.*, **87**, 559; *Chem. News*, **38**, 202) published an account of philippium, a yellow oxide characterised by a strong band in the violet,  $\lambda$  400 to 405 ( $1/\lambda^2$  625, to 623), a broad, black absorption-band in the indigo-blue,  $\lambda$  about 450 ( $1/\lambda^2$  494), two rather fine bands in the green, and one in the red.

The history of philippium is curious, and I may perhaps be allowed to give it in some detail. A year after Delafontaine's discovery Soret (*Compt. rend.*, **89**, 521; *Chem. News*, **40**, 147) published a paper in which he declared that philippia was identical with his earth X. The next month, in a note on erbia, Clève (*Compt. rend.*, **89**, 708; *Chem. News*, **40**, 224) said he could not identify Soret's X with Delafontaine's philippia, as the latter was characterised by an absorption-band in the blue which occupied the same place as one of the erbia bands. In February, 1880 (*Compt. rend.*, **90**, 221; *Chem. News*, **41**, 72), Delafontaine returned to the subject, enumerating 10 new earths in gadolinite and samarskite, viz., mosandra, philippia,

ytterbia, decipia, scandia, holmia, thulia, samaria, and two others unnamed. He said that the properties of philippia were those of Soret's X and of Clève's holmia, and proposed that the name "holmia," being a duplicate name for an already known earth, should be discarded in favour of philippia. In July, 1880 (*Compt. rend.*, **91**, 328; *Chem. News*, **42**, 185). Clève repeated his former statement that philippia was not the same body as Soret's X or holmia. Delafontaine next withdrew all he had said about the absorption-spectrum of philippium, and decided that it had no absorption-spectrum (*Archives de Genève* [3], **999**, 15). Finally, Roscoe (*Chem. Soc. J.*, **12**, 277), in an elaborate chemical examination of the earth-metals in samarskite, proved that philippia was a mixture of yttria and terbia. From a prolonged chemical study of these earths I have since come to a similar conclusion; but a spectroscopic examination of the earth left on igniting some specially purified crystals of "philippium formate" tested in the radiant matter tube, has shown me that in the separation of Delafontaine's philippium the yttria undergoes a partial fractionation, and three of its components or meta-elements,  $G\zeta$ ,  $G\hat{\zeta}$ , and  $G\beta$ , are present in great abundance, while others,  $G\alpha$  and  $G\eta$ , are almost if not quite absent.

Shortly after the announcement of philippium, Soret (*Compt. rend.*, **86**, 1062) described an earth which he provisionally called X. This was soon found to be identical with an earth subsequently discovered by Clève (*Compt. rend.*, **89**, 479; *Chem. News*, **40**, 125), and called by him holmia. Soret admitted the identity, and agreed to adopt Clève's name of holmia. Fig. 9 shows the absorption-spectrum of X or holmia. It consists of a very strong band in the extreme red,  $\lambda$  804 ( $1/\lambda^2$  155), two characteristic bands in the orange and green,  $\lambda$  640 and 536 ( $1/\lambda^2$  244 and 347), besides fainter lines in the more refrangible part of the spectrum, and a number of bands in the ultra-violet.

Simultaneously with the discovery of holmia, Clève announced the existence of a second earth from erbia, which he called thulia. Fig. 10 shows the absorption-spectrum of thulia. It consists of a very strong band in the red,  $\lambda$  680 to 707 ( $1/\lambda^2$  216 to 200), and one in the blue,  $\lambda$  464.5 ( $1/\lambda^2$  462). The residual erbia, after separation of these earths, gives a simpler absorption-spectrum, shown in Fig. 11.

In 1886 (*Compt. rend.*, **102**, 1003, 1005) Lecoq de Boisbandran showed by fractional precipitation of Soret's X and by spectroscopic examination of the simple fractions, that this X, or holmium, consisted of at least two elements, one of which he named dysprosium, retaining the name of holmium for the residue left after deducting dysprosium. Fig. 11 shows the absorption-spectrum of dysprosium; it has four bands,  $\lambda$  451.5, 475, 756.5, 427.5 ( $1/\lambda^2$  490.5, 443, 175,

547). The new holmium gives an absorption-spectrum shown in Fig. 13.

As regards dysprosium, I pointed out (*Proc. Roy. Soc.*, **40**, 502), at the time it was first announced, that I had obtained a solution in which one of the bands claimed for dysprosium, the one at  $\lambda$  451.5 ( $1/\lambda^2$  490.5), was very strong, while the others were absent. As M. de Boisbaudran associates the bands at  $\lambda$  475 ( $1/\lambda^2$  443) and  $\lambda$  451.5 ( $1/\lambda^2$  490.5) as both belonging to dysprosium, and as I have obtained an earth which gives  $\lambda$  451.5 ( $1/\lambda^2$  490.5) strong with no trace of  $\lambda$  475 ( $1/\lambda^2$  443), it is evident that the conclusion I arrived at in 1886—that dysprosium itself consisted of at least two simpler bodies—is correct.

The old spectrum of erbium (Fig. 8) shows two faint bands at  $\lambda$  550 and  $\lambda$  493 ( $1/\lambda^2$  331 and 409); the second being broader than the first. These bands do not occur in the spectra of holmium, thulium, dysprosium, or the new erbium. In a long-continued fractionation of the erbia group of earths, carried out with an ample supply of the old erbia, I find an earth giving these two bands concentrating at one end, and the bands become stronger. At the same time two other new bands are making their appearance. This, therefore, points to the existence of still another earth belonging to the erbium group.

### *Incandescence Spectra.*

Another distinct method of spectrum analysis depends on the examination of the spectrum of the light emitted by a solid substance when raised to incandescence. Almost the only known example of this is obtained in the case of erbia (*ibid.*, **40**, 77, January 21, 1886). It is scarcely known that if erbia in the solid state is illuminated by the electric or other bright light, and examined in the spectroscope, it gives a spectrum of black lines and bands as distinct as the Fraunhofer lines. The spectrum of bright lines emitted when solid erbia is heated to incandescence in the blowpipe flame has been more often observed; in this case the lines come out luminous on a faintly continuous background, whilst the reflection spectrum just mentioned is composed of black lines sharply defined and much more luminous, upon a continuous spectrum. Holmia and thulia, components of old erbia, possess a similar property (*Chem. News*, **56**, 165).

### *Phosphorescence Spectra.*

I will now deal with phosphorescence spectra. Not a few chemists and physicists, conspicuous among whom is Ed. Becquerel, have carefully studied the phenomena of phosphorescence. Phosphor-

escence may be excited by elevation of temperature, by mechanical action, by electricity, and by exposure to the rays of the sun, and the light thus given off—for example, in the case of fluorspar, has been examined by means of the spectroscope. In my own spectroscopic research I have dealt with the phosphorescence occasioned by the impact of the molecules of radiant matter upon certain phosphorescent bodies, or what I have ventured to call molecular bombardment.

It is not necessary for me to describe the mode of procedure further than to say that the substance under examination is placed in a very high vacuum—a vacuum which varies in degree in the case of certain earths. Fig. 14 shows the form of radiant matter tube I prefer. In such a vacuum, when submitted to the action of the induction current, substances phosphoresce very differently from what they do when treated similarly at the ordinary pressure of the atmosphere. Under such circumstances the spectroscopic examination of matter affords what I have called the radiant matter test. The number of substances which are thus phosphorescent is very considerable. Glass of different kinds, according to its composition, phosphoresces with various colours. Phenakite (glucinium silicate) phosphoresces blue; spodumene (aluminium and lithium silicate) gives off a rich golden-yellow light, whilst the emerald phosphoresces crimson, and the diamond, being exceptionally sensitive and brilliant, throws off a bright, greenish-white light.

The ruby, one of the minerals I examined earliest in this manner, glows with a rich, brilliant, red tone, quite independent, as regards its depth and intensity, of the colour of the stone as seen by daylight; the pale, almost colourless specimens, and the highly prized variety of the true “pigeon’s blood,” all phosphoresce with substantially the same colour.

There are several varieties of phosphorescence spectra, or rather, substances to be submitted to the radiant matter; may be previously prepared in divers manner, so as to give modified results. Thus—

*a.* An earth alone—of course in the solid state—may be very strongly ignited, and, when cold, examined in the radiant matter tube. This method differs from the use of the spectrum of incandescent solids above noticed, solely in the final test of molecular bombardment. Of this variety of phosphorescence spectra, we may take, as examples, the phenomena yielded by alumina, yttria, didymia, and lanthana.

*b.* Another modification applicable in the treatment of the less pure earths takes as material the sulphates of the earths. The substance under examination is first treated with strong sulphuric acid; the excess of the acid is then removed by heat, and, lastly, the sul-

phate is heated to a point just short of driving off all the sulphuric acid. It is then placed in the radiant matter tube, and when the exhaustion has been carried as far as necessary, the induction current is passed through (*Phil. Trans.*, Part III, May, 1883). This method gives a spectrum of broad bands, easily recognised, but by no means easy to measure. The spectroscope used should have a low dispersive power, and should not have a very narrow slit. In the case of yttrium sulphate the bands are more analogous to the absorption-bands seen in solutions of didymium than to the lines given by spark spectra. If examined with a high magnifying power the outlines of the bands become less definite. The bands are seen much more sharply when the current first passes than after it has been passing for some time and the earth has become hot. On cooling, the bands again appear sharply defined.

This method of observing the constitution of the rare earths, duly aided by delicate and prolonged chemical processes, has permitted us to push our investigations further than had previously seemed practicable. It enables us to determine whether we have reached the end of our investigations—a consummation which had hitherto been vainly sought. It has enabled us to prove that yttrium, samarium, &c., are not simple, homogeneous bodies. But what of the constituents into which they have been thus resolved? Suppose we refine them down until each displays merely one spectral band—what then? Is each one of such bodies barely differentiated from its neighbours chemically or physically, entitled to rank as an element? If so, as I pointed out in the Address which I had the honour to deliver before you in March last, we shall have to deal with further perplexing questions, arising in part from the relation of such elements to the periodic system. In a discussion of the elements, not as yet published, Dr. Wundt maintains that their possible number cannot exceed 79. But I myself see no definite and sufficient reason for limitation to this number. If these bodies are not elementary, possessing as they do the properties commonly regarded as characteristic of an element, we must be prepared to show why not?

Whatever rank may ultimately be assigned to these substances, they must, for convenience sake, have names as soon as our knowledge of their properties is in a sufficiently advanced state to allow of their removal from the suspense account.

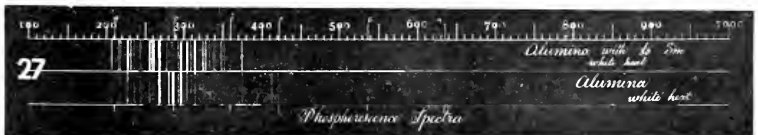
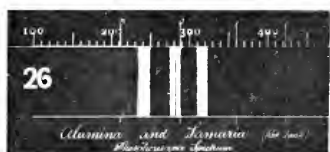
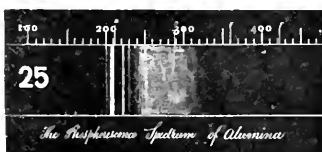
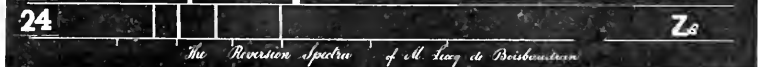
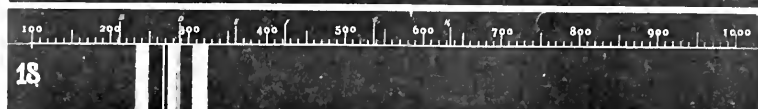
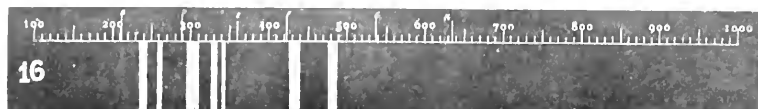
### *The Yttrium Group.*

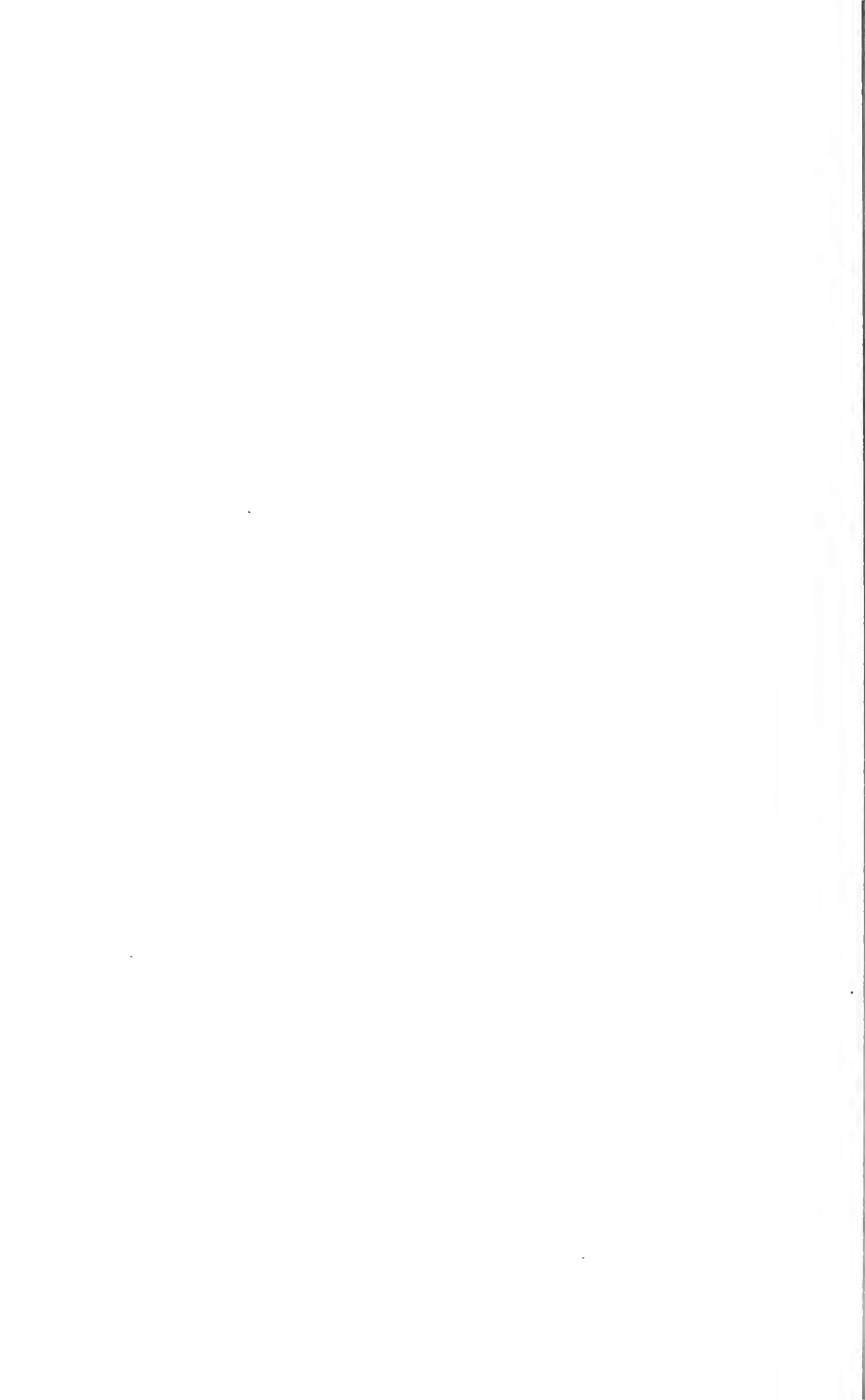
Yttrium—the old yttrium—proves now to be not a simple element, but a highly complex substance. I have come to the conclusion that it may be split up certainly into five and probably into six con-

stituents. Its phosphorescence spectrum is shown in Fig. 16, and the different bands are designated by certain letters. Fig. 17 shows the simple spectra of the separate components into which yttria can be separated by fractionation. If we take these constituents in the order of their approximate basicity—the chemical analogue of refrangibility—the lowest of these constituents gives a deep blue band,  $G\alpha$ ; then follows a strong citron band,  $G\hat{\epsilon}$ , which increases in sharpness until it may be called a line; then a red band,  $G\zeta$ ; then a deeper red band,  $G\eta$ ; and lastly a close pair of greenish-blue lines,  $G\beta$ . Following these are frequently seen  $G\epsilon$ ,  $G\gamma$ , and  $G\theta$ , the yellow, green, and red components of samarium, Fig. 19.

As the result of many years' work and several thousand fractionations of old yttria, I exhibit the series of 19 phosphorescence spectra shown on Diagram 28. The centre spectrum, marked J, is approximately that given by the crude earth, although this differs slightly according to the mineral from which it is extracted. After a time, fractionation splits the earth J into two earths, I and K, giving slightly different spectra. Fractionating I gives H and J, whilst K on fractionation yields J and L. The state of separation to which the meta-elements of the samarskite earths may be brought after many years' work is seen by the series of 19 spectra selected to illustrate the progress of the work. It must not, however, be thought that there is so great a difference between any two adjacent spectra as is here shown. To make the diagram more accurately represent what actually occurs in the laboratory it would be necessary to place between each of these 19 spectra about 1000 intermediate spectra.

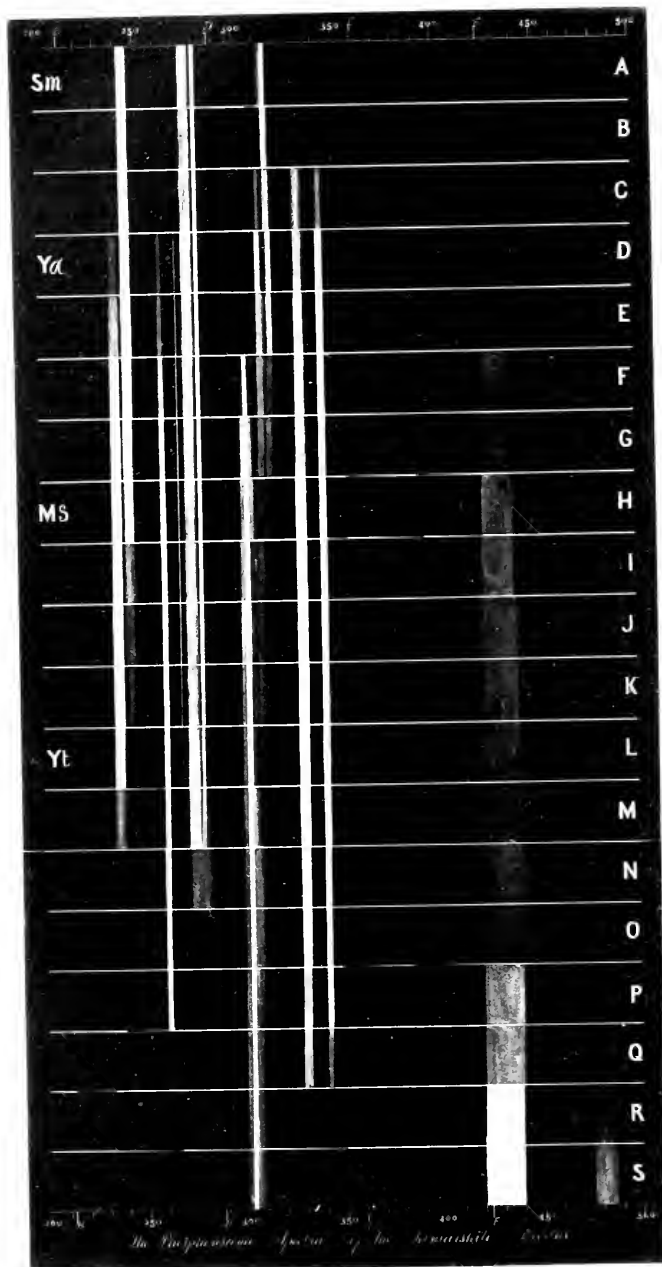
Beginning at the extreme red it will be seen that a strong band at  $\lambda$  647 ( $1/\lambda^2$  239) is of maximum intensity from G to K, when it rapidly disappears and is not seen beyond C and N. The meta-element giving this band I have called  $G\eta$ . The next band in the red  $\lambda$  639 ( $1/\lambda^2$  245), is at its maximum at A or even above, while it fades out between K and L. The next band at  $\lambda$  619 ( $1/\lambda^2$  261) has its maximum between I and O, fading out rapidly below, but being more persistent above. The meta-element to which this band is due I have called  $G\zeta$ . I next come to an extremely sharp band at  $\lambda$  609 ( $1/\lambda^2$  269), which appears to belong to an earth absent in gadolinite and present in samarskite and a few other minerals. Its greatest brilliancy is between E and K, dying away rapidly on either side. This meta-element I have called  $S\hat{\epsilon}$ . A double orange band follows, and there are indications that its two components are separable, although they must be very closely associated. The maximum brightness of the first component,  $\lambda$  603 ( $1/\lambda^2$  275), extends from O to the top of the diagram. The second component,  $\lambda$  597 ( $1/\lambda^2$  280), begins to lose brilliancy about G, and, like its companion, is at its greatest brightness at the highest spectrum











shown on the diagram. This band has been almost isolated in a specimen of crude lanthana. I have called its meta-element  $G_c$ .

The next band in order is the citron or  $G\delta$  band,  $\lambda 574$  ( $1/\lambda^2$  303.5), the most prominent in the spectrum of old yttrium. This band extends with almost undiminished sharpness and brilliancy from G to S; above G it fades out rapidly, and from D upwards it is absent. Following the citron band is a double green band. This, like the orange band just described, is separable into two components. The first, at  $\lambda 568$  ( $1/\lambda^2$  310), is almost absent in A, attains its maximum in about D, and fades out entirely at K. The second component of this green pair,  $\lambda 563$  ( $1/\lambda^2$  315), is at its maximum at A and above, and extends only to H. The meta-element giving rise to this pair I have called  $G\gamma$ . Next in order comes a pair of bright green bands. The two components  $\lambda 550, 541$  ( $1/\lambda^2$  331, 342) have not yet shown signs of dividing. The first appearance of this double band is at B, it attains its maximum at about E, and continues with almost undiminished brightness to Q. The body giving this double green band is the most persistent of all the meta-elements of these earths. I have provisionally called it  $G\beta$ .

After a dark interval a broad, hazy, double blue band is seen, having its centre at  $\lambda 482$  ( $1/\lambda^2$  430.5). This band, first appearing at about F, increases in brightness down to the last fraction at S. Its meta-element is called  $G\alpha$ . Lastly, at  $\lambda 456$  ( $1/\lambda^2$  481), is seen a deep violet band, coming in first at Q, and getting brighter as we get lower down the fractionations. This band is of extraordinary brilliancy in some samples of ytterbia, but as it is absent in a specimen of ytterbia from Nilson, said by him to be perfectly pure, it is probably due to some other new body which I have therefore named provisionally  $S\gamma$ .

Although, for economy of space, it is inconvenient to represent a longer series than is here shown, my fractionations have been pushed far beyond the limits shown on the diagram. Fractions above A and below S give ample evidence that the process of differentiation has not reached its utmost limit.

On the left of the diagram, Fig. 28, I have attached chemical symbols to some of the spectra. Thus the top spectrum, A, is the one shown by samarium. At D is the spectrum given by Marignac's  $Y\alpha$  or gadolinium. At H is seen the spectrum of mosandrum, and at L is shown the spectrum given by what would ordinarily be called pure yttrium. A study of this diagram will, I think, convince any impartial observer that the lessons it conveys fully bear out my contention that samarium, gadolinium, mosandrum, and yttrium, are not actual chemical elements, but are compounded of certain simpler bodies which may conveniently be called "meta-elements."

A possible explanation of the existence and nature of the new bodies into which "old yttrium" has been split up, and of parallel cases which will doubtless be found on closer examination, is this. Our notions of a chemical element must be enlarged; hitherto the elemental molecule has been regarded as an aggregate of two or more atoms, and no account has been taken of the manner in which these atoms have been agglomerated. The structure of a chemical element is certainly more complicated than has hitherto been supposed. We may reasonably suspect that between the molecules we are accustomed to deal with in chemical reactions, and the component or ultimate atoms, there intervene sub-molecules, sub-aggregates of atoms, or meta-elements, differing from each other according to the position they occupy in the very complex structure known as "old yttrium."

The arguments in favour of the different theories are as yet not unequally balanced. But the assumption of compound molecules will perhaps account for the facts, and thus legitimate itself as a good working hypothesis, whilst it does not seem so bold an alternative as the assumption of eight or nine new elements.

The history of the examination of the rare earths and of its results would lack completeness and intelligibility did I not refer to the views taken by my distinguished friend M. Lecoq de Boisbandran.

In a communication to the Academy of Sciences this eminent chemist says (*Compt. rend.*, **100**, 1437): "It is a singular fact that the positions of the phosphorescence bands observed by Mr. Crookes with very pure compounds of yttrium are sufficiently near those which I, on my part, have obtained with the hydrochloric solutions of earths separated as far as possible from yttria, chemically as well as spectroscopically. My reversion spectrum cannot, I think, be attributed to yttrium, for on the one hand it is seen *brilliantly* with products which give no trace of yttrium rays with the direct spark, and on the other hand, I have found it impossible to obtain it sharply from certain earths extremely rich in yttria."

M. de Boisbandran further states in a note:—"This spectrum (*i.e.*, the one which he had just described) is now recognised as being identical with that which is ascribed to pure yttria by Mr. Crookes, and which this *savant* obtained under experimental conditions very different from mine. Nevertheless, my latest observations, as well as earlier ones, lead to the conclusion that yttria is not the cause of the spectrum bands observed. In my fractionations the phosphorescence spectrum gradually gets weaker as I advance towards the yttria end. With almost pure yttria the phosphorescent bands show themselves faintly or not at all, whilst they are brilliant with the earths which do not give by the direct spark the rays of yttrium to any appreciable extent."

It will, I think, appear that the issue between myself and M. de Boisbaudran turns on the question: What is yttria? To what substance can this name be legitimately given? A short time ago the name conveyed to all chemists only one meaning, perfectly definite and undisputed. I have received specimens of yttria from M. de Marignac, considered by him to be purer than any which had ever been previously prepared; from Professor Clève (called by him *purissimum*); and from M. de Boisbaudran, which he pronounces to be yttria "scarcely soiled by traces of other earths." Along with these I have specimens prepared by myself and purified up to the highest point known. A very short time ago every living chemist would have called these samples "yttria." Moreover, they all give my phosphorescence spectrum *in vacuo* with such intensity that such phosphorescence cannot be rationally ascribed to slight traces of impurities.

This substance, like other chemists, I formerly called "yttria," but since its complex nature has been ascertained I speak of it as "*old* yttria."

M. de Boisbaudran, however, inadvertently uses the word in a manner not quite free from ambiguity. By "yttria," I repeat that I mean now, and have always meant, the yttria of Clève, of Marignac, and of all chemists up to the beginning of the year 1886, the yttria whose metallic basis has the approximate atomic weight of 89. M. de Boisbaudran at one time writes as if our meanings were identical: "It is certain," he says, "that my earth, very rich in yttria, gives a beautiful spectrum in the vacuum tube." Again he informs me: "M. Becquerel has recently examined my earths A and B in ultra-violet light, and has obtained results analogous to yours; that is to say, the earth rich in yttria has generally shone brighter than the other." The "earth A" here spoken of gives my phosphorescent spectrum with wonderful brilliancy, and is the one described above by M. de Boisbaudran as "yttria scarcely soiled by traces of other earths." This yttria, my distinguished friend goes on to say, "is the same as that of Clève and Marignac, varying only in slight impurities, Marignac's being perhaps the purer." So far then we agree in the meaning to be attached to the word "yttria."

But at other times M. de Boisbaudran gives the name "yttria" to an earth of quite distinct properties, to an earth he has obtained in most minute quantities after months of reiterated fractionation, which gives *no* spectrum in the vacuum tube. Here, therefore, we have the name "yttria" applied to two distinct substances, the one giving a brilliant phosphorescence spectrum, and the other giving none at all, surely a misleading ambiguity. Moreover, I am constrained to question the propriety of my friend's use of the designation "yttria"

in the latter sense. Quite recently (*Compt. rend.*, 108, 166, January 28, 1889) M. de Boisbaudran has defined his "yttria" as an earth, whether simple or complex, having a characteristic spark spectrum, but not giving a phosphorescence spectrum in the radiant matter tube or by his process of reversion, and having an atomic weight of near 89 for its metal.

Why should this non-phosphorescent earth deserve the name of elemental yttria? Why may we not just as well allot the name to some one or other of the phosphorescing earths which M. de Boisbaudran brands as impurities? It seems to me that to refine away the most characteristic attributes of a body, to call the *caput mortuum* by the original name, and pronounce everything else an "impurity," is a departure from the recognised principles of scientific reasoning and practice which it is a duty to protest against.

I have just mentioned that the earth heretofore called yttria and supposed to be simple has been split up into a number of simpler bodies. Now these constituents of the old yttria are not *impurities* in yttria any more than praseodymium and neodymium are impurities in didymium. They proceed from a real splitting up of the yttrium molecule into its components, and when this process is completed the old "yttria" has disappeared. If these newly discovered components on further examination should be found worthy to take the rank of elements I think, as first discoverer, I am entitled by the custom prevailing among men of science, to name them. For the present, and until their investigation is more advanced, I designate them by provisional symbols. One of the most distinct characteristics of "old yttria" is its very definite spark spectrum. To which of its components this spark spectrum belongs I am not yet able to say. It is possible that the particular component to which the spark spectrum is due yields no phosphorescent spectrum. It is also possible that the spark spectrum, like "old yttria," may prove to be compound, and then the well-known lines it contains will have to be shared between two or more of the newly-discovered bodies. I wish emphatically to re-state that at present no single component of old yttria can lawfully lay claim to what may be called the paternal name; and it seems to me that in the present state of the question no one is entitled to call one of the new bodies "yttria," and to characterise the remainder as impurities.

I regret to add that a misunderstanding exists between M. de Boisbaudran and myself. In a memoir presented to the Academy of Sciences on January 28th of the present year my distinguished colleague shows he completely misapprehends my position, and he so far misinterprets me as to make me say that the gadolinia or  $Y_x$  of M. de Marignac is a mixture of 61 parts of yttria and 39 parts of samaria!

But what is the fact? So far back as June 9th, 1886, I put it on record (*Proc. Roy. Soc.*, **40**, 502) that “ $Y_z$  is composed of the following band-forming bodies:— $\lambda$  [541—549], [564], [597], [609], [619], together with a little samarium. Calling samarium an impurity, it is thus seen that gadolinium is composed of at least four simple bodies.”

Again in a paper entitled “What is Yttria?” I wrote (*Chem. News*, **54**, 39, July 23, 1886)—

“Gadolinium is composed of at least four simpler bodies,  $G\beta$ ,  $G\gamma$ ,  $S\delta$ , and  $G\zeta$ ; the pair of green lines [ $\lambda$  541 and  $\lambda$  449, mean 545], being the strongest feature in its spectrum, may be taken as characteristic of gadolinium.”

“M. de Boisbaudran says:—‘Mr. Crookes appears to attribute to gadolinium the double green band.’ This is scarcely accurate; I did not ascribe the double green band to gadolinium, but finding by my test that the *so-called* gadolinium was a compound body, the earth  $G\beta$  being its strongest component, I proposed to attach the name of gadolinium to  $G\beta$  rather than give it a new name, and thus multiply names unnecessarily.”

Thus in 1886 I corrected the error which M. de Boisbaudran now repeats.

Again, I said that the work of fractionating this mixture, “*for its completion*,” would occupy a space of time in comparison with which the life of man is all too brief—a statement transformed into the assertion that to separate yttria and samaria—a relatively easy task—would take more than a life-time.

M. de Boisbaudran’s misconception is the more striking since in a foot-note he gives correctly my very words from my “Address to the Chemical Section of the British Association,” in 1886, and from the “Genesis of the Elements.” How he can have mistaken my meaning is a mystery, as he is an excellent English scholar. Certainly any reader of the *Comptes rendus* who understands English will at once see that there is no foundation for M. de Boisbaudran’s criticism.

#### *Action of Different Earths on Phosphorescence Spectra.*

Another modification of phosphorescence spectroscopy is produced by the previous addition of other earths to the specially phosphorescent earths, and of the results of such addition some instances have already been mentioned. Lime exerts in this manner a remarkable action. By itself it phosphoresces with a continuous spectrum, after the fashion of yttria with a discontinuous spectrum. If, however, they are mixed, the phosphorescing energy of the lime does not extend over the whole spectrum, but concentrates itself on strengthening the yttria bands. These bands become broader, but also less definite, in proportion as the lime increases in quantity.

Lime also may be made to play a useful part in bringing out the phosphorescent bands of samaria. The bands are not so numerous as those of yttrium, but the contrasts are sharper. Examined with a somewhat broad slit, and disregarding the fainter bands, the samarium spectrum is seen to consist of three bright bands—red, orange, and green—nearly equidistant, the orange being brightest. With a narrower slit the orange and green bands are seen to be double. (Fig. 18).

The addition of lime also affords an argument for the compound nature of samaria, as it suppresses the sharp line  $S\delta$ , the most striking feature in the phosphorescence spectrum shown by pure samarium sulphate. On the other hand, an addition of old yttria deadens the other lines of samaria, but brings out the line  $S\delta$  more strongly. Fig. 19 represents the spectra given by the meta-elements of samarium.

Lanthanum sulphate in the radiant matter tube phosphoresces with a reddish colour and has a broad hazy band in the orange, with a sharp line superposed. This line is identical with the line of  $G\epsilon$ , one of the components of the phosphorescent spectrum of samarium. If lime is added to lanthanum, the phosphorescence changes its colour from red to yellow. Lime also brings out the lines of yttrium and samarium if they are present as impurities. When  $G\delta$ ,  $G\alpha$ , and  $G\beta$  are present in small proportions with lime, the lines  $G\delta$  and  $G\alpha$  become intensified, but a dark place appears in place of the green  $G\beta$  band. Hence it appears that if only a small trace of  $G\beta$  is found with lime and lanthanum, the green line is not only obliterated, but the quenching action suppresses that part of the continuous lime spectrum which has the same refrangibility as the  $G\beta$  line, thus giving a black space in the spectrum.

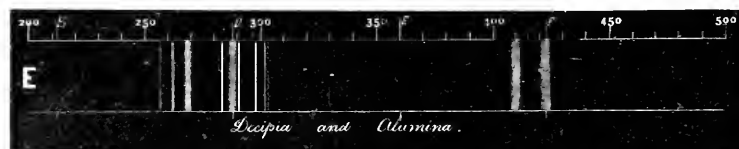
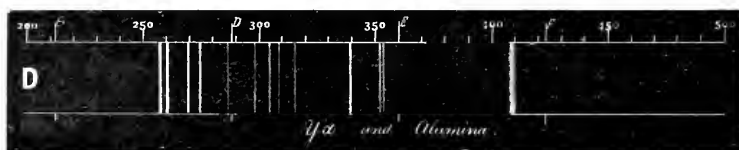
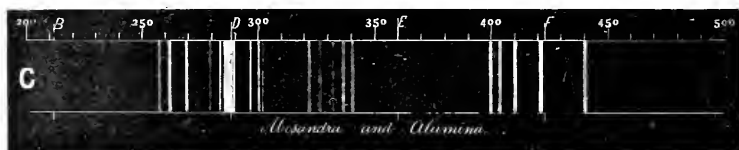
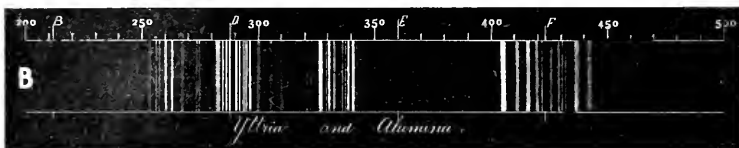
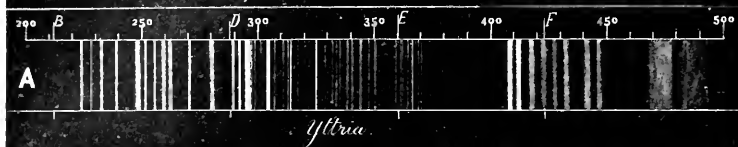
A specimen of lanthana thrown out in a fractionation of didymia, examined in the radiant matter tube, phosphoresces of a yellow surface-colour and gives an extremely brilliant spectrum (Fig. 20). In the red there is a very fine and sharp line, somewhat like the alumina line, but nearer C of hydrogen. Then come a couple of misty red lines, the first apparently compound, then a hazy pair of green lines, and finally another wide apart pair of a bluish-green; the first of these lines is intensely brilliant.

### *Interference of Phosphorescence Spectra.*

I have already frequently noted the modification induced in the normal spectrum of one earth by the mixture of various quantities of others, when treated as anhydrous sulphates; and of these one of the most striking is seen in the case of a mixture of samaria with yttria,





*New Sharp line Phosphorescence Spectra.*

since the presence of even 40 per cent. of yttria practically obliterates its spectrum. The most minute proportion of lime added to samaria causes the sharp line at  $\lambda^2$  269 in its spectrum to vanish, at the same time greatly intensifying the other bands. Strontia, baryta, glucina, thoria, magnesia, lanthana, alumina, and oxides of zinc, cadmium, lead, bismuth, and antimony, all give characteristic spectra with samaria, and have been fully described in my paper on that body (*Phil. Trans.*, Part II, 1885). The action of lime upon yttria is of great use in detecting very small quantities of this earth when in combination with other elements which otherwise would prevent its phosphorescence.

A recent discovery of some beautiful spectra given by the rare earths when their pure oxides are highly calcined, shows the remarkable changes produced in the spectra of these earths when two or more are observed in combination. It has likewise opened to me a wide field of investigation in the nature of the elements themselves. Alumina is especially active in inducing new spectra when mixed with the rare earths. I have given more than a twelvemonth to the exclusive study of alumina phosphorescence, and still the research is incomplete. But I have obtained some remarkable results. A moderate amount of fractionation has enabled me to penetrate below the surface of the red glow common to crude alumina, and to see traces of a most complicated sharp line spectrum. By pushing one particular process of fractionation to a considerable extent, I have obtained evidence of a body which is the cause of some of these lines. The spectrum, described by me in 1887 (*Chem. News*, 56, 62, 72) is one of great beauty, and a fair idea of it is given in Fig. 21. The new body is probably one of the rare elements or meta-elements closely connected with decipia, for I have reproduced the spectrum very fairly by adding decipia to alumina. Before arriving at definite conclusions much time must be devoted to the subject. Certain it is that this new earth is not yttria, erbia, samaria, didymia, lanthana, holmia, thulia, gadolinia, or ytterbia, the spectrum of each of these when mixed with alumina being very beautiful, but differing entirely from the decipia-alumina spectrum. Some of these new spectra are shown in Fig. 29.

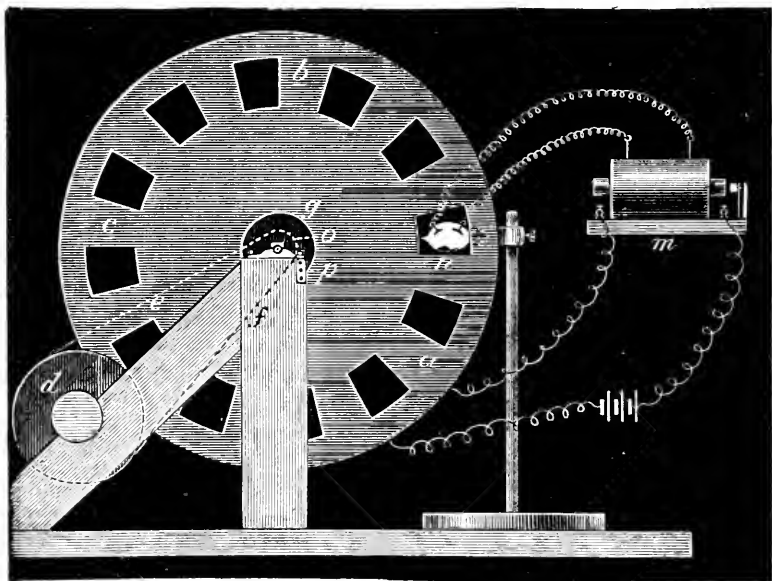
### *The Phosphoroscope.*

The phosphoroscope affords another method of verifying the simple or compound character of a substance. It is well known that the continuance of phosphorescence after the cessation of the exciting cause varies widely, from some hours, as in the case of the phosphorescent sulphides, to the fraction of a second in the case of uranium glass and quinine sulphate. On examining phosphorescent earths

glowing in a vacuum tube under the action of the induction discharge, I found remarkable differences in the duration of this residual glow. Some of the earths, after the cessation of the current, remain luminous for an hour or more, whilst others cease to phosphoresce immediately on the stoppage of the current. Take the case of yttrium. As already stated, I succeeded in resolving this earth into several simpler bodies not equal in basicity. While seeking for further proof of the distinct character of these bodies I observed that the after-glow differed somewhat in colour from that which the earth exhibited whilst the current was still passing. Further, the spectrum of the after-glow seemed to show, so far as I could judge by the faint light, that some of the lines were missing. As this phenomenon indicated another difference among the components of yttrium, I examined them in an instrument similar to Becquerel's phosphoroscope, but acting electrically instead of by means of direct light.

Without describing this apparatus, shown in Fig. 22, I may mention some of the results obtained by its use. Under ordinary circum-

FIG. 22.



stances it is scarcely possible to perceive any phosphorescence in an earth until the vacuum is so high that the line spectrum of the residual gas begins to grow faint. Up to this point, the stronger light of the glowing gas overpowers the feeble glow of the phosphorescence. But

in the phosphoroscope the light of the glowing gas lasts only for an inappreciable time, while that of the phosphorescent earth persists long enough to be distinctly observed. The different bands of the new constituents of yttria do not all appear at the same speed of rotation. At the lowest speed the double greenish-blue band of  $G\beta$  is first seen, followed next by the dark blue band of  $G\alpha$ . As the velocity increases there follows the bright citron-yellow band of  $G\delta$ , and as the utmost speed approaches the red band of  $G\zeta$  is seen, but with difficulty. If lanthanum sulphate along with a little lime is examined in the phosphoroscope the line of  $G\epsilon$  is visible at the lowest speed;  $G\delta$  follows at an interval of 0.0035 second, and the  $G\alpha$  line immediately afterwards.

*M. de Boisbaudran's Reversion Spectra.*

Another modification of the phosphorescence process is afforded by the "reversion spectra" of M. Lecoq de Boisbaudran.

The following is the description of this process by M. Lecoq de Boisbaudran, read before the Academy of Sciences on June 8th, 1885:—"When the electric spectrum of a solution *with a metallic base* is produced it is customary to make the outside platinum wire (whence the induction spark strikes) positive, the liquid consequently forming the negative pole. If the direction of the current is reversed the metallic rays (due to the free metal or to one of its compounds) are scarcely or not at all visible; at all events, so long as the exterior platinum wire now forming the negative pole is not coated with a deposit." Fig. 15 shows the arrangement. M. de Boisbaudran continues:—

"Having again taken up last year my researches on the rare earths belonging to the didymium and yttrium family, I had occasion to observe with many of my preparations the formation of spectrum bands, nebulous, but sometimes tolerably brilliant, having their origin in a thin layer of a beautiful green colour, which appeared at the surface of the liquid (a solution of a chloride) when it was rendered positive."

M. de Boisbaudran further adds:—"The production of my reversion spectrum appears to be analogous physically with the formation of the phosphorescence spectra obtained by Mr. Crookes at the negative pole in his high vacuum tubes containing certain compounds of yttria. The conditions of the two experiments are, however, practically speaking, very different."

By this method M. de Boisbaudran has discovered phosphorescent spectra, shown in Figs. 23 and 24, which he considers due to the presence of two earths, one of which, supposed to be new, he has

provisionally named  $Z\alpha$ , and another, also thought at first to be new, and therefore called  $Z\beta$ , but since admitted by him to be terbia (*Compt. rend.*, **108**, 167, Jan. 28, 1889). In the hands of so skilful an experimentalist as my accomplished friend, this method may give trustworthy indications, but the test is really beyond the range of practical analysis, owing to the difficulty of eliciting the phenomena. Unless the strength of the spark, the concentration and acidity of the solution, and the dispersive and magnifying power of the spectroscope bear a certain proportion to each other, the observer is likely to fail in seeing a spectrum even in solutions of earths which contain considerable quantities of  $Z\alpha$  and terbia.

I have had not only the advantage of personal instruction in Paris from M. de Boisbaudran himself in the best methods of getting these reversion spectra, but I secured some of the identical earths which give these spectra most distinctly. Yet with all these advantages I have experimented for hours together without being able to see more than a feeble glimmer of the bands described by M. de Boisbaudran. Moreover, the bands of these "reversion" spectra, at their strongest, are but faint and hazy substitutes for the brilliant lines of yttria seen by the "bombardment" process, and they do not even in all cases agree with them in position. M. de Boisbaudran, speaking of the relative sensitiveness of our two processes, admits that the bombardment process *in vacuo* is incomparably more delicate than his reversion method. My own estimate of the relative sensitiveness of the two methods is in the proportion of at least 1 : 100. Though so accurate an observer, M. de Boisbaudran concluded apparently too hastily that two spectra are identical, when one of them has been measured only approximately, and contains bands in positions which are perfectly blank in the other.

### *The Phosphorescence of Alumina.*

I now wish to draw attention to some recent researches on the phosphorescence spectrum given by alumina. So far back as 1859 Becquerel examined in his phosphoroscope pure alumina carefully prepared, and described it as glowing with a splendid red colour. He rendered his specimens phosphorescent by exposure to the sun, and made no use of the induction spark. As described by Becquerel (*Ann. Chem. Phys.*, **57**, 50, 1859), the spectrum of the red light emitted from alumina agrees with that of the ruby when submitted to the radiant matter test. It displays one intensely red line a little below the fixed line B in the spectrum, having a wave-length of about 689.5. There is a continuous spectrum beginning at about B and a few fainter lines beyond it, but in comparison with this red line the

faint ones are so dim that they may be neglected. My latest observations in the vacuum tube prove this line to be double, the distance apart of the components being about half the distance separating the D lines (*Proc. Roy. Soc.*, **42**, 26, Dec. 30, 1886), their respective wave-lengths being 694.2 and 693.7 ( $1/\lambda^2$  207.5 and 207.8). This alumina spectrum is shown in Fig. 25.

The red phosphorescence of this alumina is exceedingly characteristic. M. de Boisbandran (*Compt. rend.*, **103**, 1107; **104**, 330, 478, 554, 824) contends, however, that this red phosphorescence is due not to the alumina itself, but to an accompanying trace of chromium,  $\frac{1}{1100}$ th part of chromium being sufficient to give a splendid red phosphorescence, whilst even 1 part of chromic oxide in 10,000 will produce a very distinct rose colour. In testing this view I have purified alumina most carefully, so as to secure the absence of chromium, and on examining it in the radiant matter tube I have still obtained the characteristic phosphorescence and spectrum. I have then added to my purified alumina chromium in known varying proportions, but without finding any increase in the intensity of the phosphorescence. I fractionated my purified alumina by different methods and found that the substance which forms the crimson line becomes concentrated towards one end of the fractionations, whilst chromium concentrates at the other end. I have suggested four possible explanations of the phenomena—

1. The crimson line belongs to alumina, but it is liable to be masked or extinguished by some other earth, which accumulates towards one end of the fractionations.

2. The crimson line is not due to alumina, but to the presence of an accompanying earth, which accumulates towards the other end of the fractionations.

3. The crimson line belongs to alumina, but its development requires certain precautions to be taken in the duration and intensity of the ignition, and absolute freedom from alkaline and other bodies carried down by precipitated alumina, and difficult of removal by washing.

4. The earth alumina is a compound molecule, one only of its component sub-molecules giving the crimson line. If this hypothesis is correct, alumina must admit of being split up in a manner analogous to yttria.

#### *Sharp Line Spectra with Phosphorescent Alumina.*

About 18 months ago M. de Boisbandran published some results on "New Fluorescence with well-defined Spectral Rays" (*Compt. rend.*, **105**, 258). Having mixed alumina with 2 per cent. of samaria

and converted the mixture into sulphate, he heated it to a temperature between the melting point of copper and silver. This product, examined in the radiant matter tube, gives a faint fluorescence, the spectrum resembling the samarium-aluminium spectrum described by me in June, 1885 (*Phil. Trans.*, Part II, 1885, 712) (Fig. 26). That is, aluminium and samarium give a spectrum resembling the corresponding calcium-samarium one as to the red and the double orange, but having a very broad, rather faint, green band with a black division in the middle occupying the position of the bright green band of calcium-samarium.

On submitting this aluminium-samarium mixture to a very high temperature, M. de Boisbandran finds that its spectrum alters greatly. In place of the three nebulous bands, there are now a number of sharp rays forming three groups corresponding respectively to each of the three diffused bands above described.

This spectrum seems to me closely to resemble the complicated system of sharp lines shown by alumina after moderate fractionation, to which I have already referred (Fig. 27, lower spectrum). Taking some of this alumina, I added to it one-fiftieth of its weight of samaria, and thereby obtained a spectrum similar to that described by M. de Boisbandran (Fig. 27, upper spectrum). As I had suspected, the two spectra are almost identical; the effect of the samaria is simply to intensify some of the lines and weaken others. But between this sharp line high temperature spectrum and the band spectrum (Fig. 26) given by the same mixture treated at a lower temperature I fail to see any such resemblance as could support the view that the groups correspond save that "those of the line spectra are less refrangible." The explanation of M. de Boisbandran's result is simple. Both samarium sulphate and aluminium sulphate resist a red heat without their sulphuric acid being driven off. Aluminium sulphate does not phosphoresce, samarium sulphate does, therefore the mixture gives the samarium spectrum. But if the mixed sulphates are heated to the highest blowpipe temperature both are decomposed, and there is left a mixture of samaria and alumina. Now, samaria by itself gives no phosphorescence spectrum, but alumina gives the new line spectrum I have described.

This method is applicable only when the earths are in a sufficiently high state of purity. The presence of exceedingly small traces of other matter may greatly modify the spectrum.

### *Conclusions.*

During the course of the investigations—whose results are briefly summarised in the foregoing pages,—I have repeatedly had recourse



to the balance, to ascertain how the atomic weights of the earths under treatment were varying. An atomic weight determination is valuable in telling when a stable molecular grouping is arrived at. During a fractionation, the atomic weight of the earth slowly rises or falls until it becomes stationary, after which no further fractionation of that lot *by the same process* makes it vary. Usually a result of this kind has been relied on as proof that the elementary stage has been reached. This constancy of atomic weight, however, only proves that the original body has been split up by the fractionating process into two molecular groupings capable of resisting further decomposition by that identical process; but these groupings are not unlikely to break up when a different fractionating process is brought to bear on them, as I found in the separation of didymium and samarium when using dilute ammonia as the fractionating precipitant. In my paper on "Radiant Matter Spectroscopy" I said\*:—"After a time a balance seems to be established between the affinities at work, when the earth would appear in the same proportion in the precipitate and the solution. At this stage they were thrown down by ammonia, and the precipitated earths set aside to be worked up by the fusion of their anhydrous nitrates so as to alter the ratio between them, when fractionation by ammonia could be again employed."

It is obvious that when the balance of affinities here spoken of was reached, the atomic weight of the mixture under treatment would have become constant, and no further fractionation would have caused the atomic weight to alter.

Atomic weight determinations are valuable in telling when the fractionating operation in use has effected all the separation it can: at this point it becomes constant. The true inference is, not that a new earth has been obtained, but simply that the fractionating operation requires changing for another, which will cleave the group of meta-elements in a different direction.

Meantime, I have kept strictly in view the question, What is an element, and how shall it be recognised when met?

On this subject I beg to submit the following considerations, which, primarily referring to didymium, may at any moment apply to other cases:—

Neodymium and praseodymium are simply the products into which didymium is split up by one particular method of attack.

It must be remembered that a single operation, be it crystallisation, precipitation, fusion, partial solution, &c., can only separate a mixture of several bodies into two parts, just as the addition of a reagent only divides a mixture into two portions, a precipitate and a

\* "Part II, Samarium," *Phil. Trans.*, Part II, 129, June 18, 1885.

solution, and these divisions will be effected on different lines according to the reagent employed. We add, *e.g.*, ammonia to a mixture, and at once get a separation into two parts. Or we add, say, oxalic acid to the same original solution, and we then split up the mixture into two other parts differently arranged.

Thus by crystallising didymium nitrate (in Auer's way) we divide the components into two parts. By fusing didymium nitrate we divide its components in a different way; but so long as different methods of attack split up a body differently, it is evident that we have not yet got down to "bed rock."

Further, a compound molecule may easily act as an element. Take the case of didymium, which is certainly a compound, whether the products of Auer's operation be final or not. Didymium has a definite atomic weight; it has well-defined salts, and has been subjected to the closest scrutiny by some of the ablest chemists in the world. I refer particularly to Clève's classical memoir. Still the compound molecule known as didymium was first too firmly held together to act otherwise than as an element, and as a seeming element it emerged from every trial. The simple operations to which it had been submitted in the preparation of its salts, and in its purification from other compound molecules, such as samarium and lanthanum, were not sufficient to split it up further. But subjected to a new method of attack it decomposes at once.

We have, in fact, a certain number of reagents, operations, processes, &c., in use. If a body resist all these and behave otherwise as a simple substance, we are apt to take it at its own valuation and to call it an element. But for all that, it may, as we see, be compound, and as soon as a new and appropriate method of attack is devised we find it can be split up with comparative ease. Still, we must never forget that, however complex, it can hardly be resolved into more than two parts at one operation.

From considerations above laid down I do not feel in a position to recognise neodymium and praseodymium as elements. We need some criterion for an element which shall appeal to our reason more clearly than the old untrustworthy characteristic of having not as yet been decomposed, and to this point I must beg to call the special attention of my colleagues. It may be that whatever body gives only one absorption-band is an element, but we cannot conversely say that an element may be known by its giving only one absorption-band, since most of our elements give no bands at all!

Until these important and difficult questions can be decided, I have preferred to open what may be figuratively called a suspense account, wherein, as I have previously suggested, we may provisionally enter all these doubtful bodies as "meta-elements."

But these meta-elements may have more than a mere provisional value. Besides compounds, we have hitherto recognised merely ultimate atoms, or the aggregations of such atoms into simple molecules. But it becomes more and more probable that between the atom and the compound we have a gradation of molecules of different ranks, which, as we have seen, may pass for simple elementary bodies. It might be the easier plan, so soon as a constituent of these earths can be found to be chemically and spectroscopically distinguishable from its next of kin, to give it a name, and to claim for it elemental rank; but it seems to me the duty of a man of science to treat every subject, not in the manner which may earn for him the greatest temporary *κῆδος*, but in that which will be of most service to Science.

If the study of the rare earths leads us to clearer views on the nature of the elements, neither my colleagues nor myself will, I am sure, regret the months spent in tedious and apparently wearisome fractionations. No one can be more conscious than myself how much ground is yet uncovered and how many radical questions have received but very inadequate answers. But we can only work on, "unresting, unhalting," trusting that in the end our work will throw some white light upon this deeply interesting department of chemical physics.

Throughout the address, attention was directed to the various spectra, and to the methods of producing them; the action of different earths, &c., on phosphorescence spectra was also specially considered.

Professor Dewar proposed a vote of thanks to the President, coupled with the request that he allow his address to be printed; Dr. Gladstone seconded the motion, which was carried by acclamation. The President briefly responded.

Dr. Russell, the Treasurer, then gave an account of the financial position of the Society. The receipts by admission fees and subscriptions had been £3,402; by sale of Journal, £365 3s. 3d.; and by dividends on invested capital, £344 4s. 3d. The expenses on account of the Journal had been £2,350 5s. 11d.; on account of the Abstracts of Proceedings, £164 4s. 7d.; on account of the Library, £308 5s. 6d.; the total expenditure being £3,429 18s. 3d. £500 had been invested in Metropolitan Board of Works  $3\frac{1}{2}$  per cent. stock, and the balance in hand was £1,833 10s. 6d., the balance at the corresponding period last year having been £1,672 19s. 3d.

Professor Thorpe moved that the thanks of the Society be tendered to the Treasurer for his services during the past session; Dr. Perkin seconded the motion. Dr. Russell, after replying, proposed a vote of

	£	s.	d.	£	s.	d.	Expenses on Account of the Journal.	£	s.	d.
Balance at Bank March 21st, 1887	1,672	12	0	1,672	19	3	Salary of the Editor	250	0	0
in hands of Treasurer		7	3				Salary of the Sub-Editor	162	10	0
							Miscellaneous Expenses of Editor	3	17	4
							Fees to Abstractors	307	13	5
							Printing of Journal	1,354	19	10
							Distribution of Journal	298	5	4
								2,358	5	11
							Expenses on Account of the Library.			
							Salary of Librarian	50	0	0
							Library Attendant	62	6	0
							Books and Periodicals	166	1	11
							Binding	30	3	7
							Printing Author's Copies	308	5	6
							Proceedings of Royal Society	43	5	0
							Distribution of Proceedings of Royal Society	60	0	0
							Printing and Distribution of Abstracts of Proceedings	2	4	11
							Miscellaneous Printing	162	10	0
							Inhabited House Duty and Income-tax	70	11	6
							Stationery	8	1	3
							Expenses connected with Prof. Rucker's Lecture	31	0	0
							Repairs	1	5	0
							Longstaff Metal	18	6	10
							Collector's Commission on Subscriptions	1	5	0
							Treasurer's Stamps and Drafts, and Charges on Drafts	169	18	0
								5	8	2
							House Expenses.			
							Providing Refreshments	17	3	3
							Heating the Building	26	16	0
							Lighting	52	0	0
							Cleaning	20	0	0
							Petty House Expenses	9	12	10
							Wages of House Porter	58	10	0
								184	2	1
							Treasurer's Petty Cash Disbursements	3	14	6
							Purchase of £300 Metropolitan Board of Works 3½ per cent. Stock	560	13	0
							Balance at Bank	1,831	17	9
							in hands of Treasurer	1	12	9
								1,833	10	6
								5,824	1	9

Audited and found cor-  
rect.  
March 22nd, 1889.

ROBERT H. DAVIES,  
R. J. FRISWELL,  
SAMUEL RIDEAL.

	£	s.	d.	
Balance at Bank .....	1,831	17	9	
"    in hands of Treasurer .....		1	12	9
Consols (Converted) .....	4,000	0	0	
London and North Western Railway Debenture Stock .....	788	0	0	
Metropolitan Board of Works 2½ per cent. Stock .....	5,600	0	0	

Assets.

	£	s.	d.
Dividends on Consols.			
Metropolitan Board of Works 3½ per cent. Stock	186	12	11
London and North Western Railway			
Debenture Stock	30	13	10
Bonus on Conversion of Consols	10	0	0

	£	s.	d.
Balance at Bank March 21st, 1887	1,672	12	0
in hands of Treasurer		7	3
	1,672	19	3
Receipts by Admission Fees, Subscriptions, and Life Compositions, from March 21st, 1888, to March 18th, 1889.			
16 Life Compositions	320	0	0
141 Admission Fees	561	0	0
25 Subscriptions for 1886	50	0	0
82 " " 1887	161	0	0
317 " " 1888	746	0	0
795 " " 1889	1,556	0	0
1 " " 1890	2	0	0
	3,402	0	0
Sale of Journal and Index	365	3	3
Subscriptions for Proceedings of Royal Society	21	10	0
from Institute of Chemistry	7	13	0
from Society of Public Analysts	4	4	0
from Chemical Industry	6	6	0

TREASURER OF THE CHEMICAL SOCIETY IN ACCOUNT WITH RESEARCH FUND.  
 FROM MARCH 21ST, 1888, TILL MARCH 18TH, 1889.

Dr.

CR.

1888.		£	s.	d.
Mar. 21.	Balance at Bank .....	309	11	5
	Dividends on Metropolitan Board of Works 3½ per cent. Stock .....	136	7	2
	Dividends on North British Railway Stock..	38	17	9
		<hr/>	<hr/>	<hr/>
		484	16	4
	Honorarium with Longstaff Medal .....			
	Balance at Bank .....	464	16	4
		<hr/>	<hr/>	<hr/>
		£484	16	4

<i>Assets.</i>	<i>£</i>	<i>s.</i>	<i>d.</i>
North British Railway 4 per cent. Stock ..	1,000	0	0
Metropolitan Board of Works Stock.....	4,000	0	0
Balance at Bank .....	464	16	4
	<hr/>		
	£5,164	16	4

Audited and found correct,  
March 22<sup>nd</sup>, 1889.

ROBERT H. DAVIES,  
R. J. FRISWELL,  
SAMUEL RIDEAL.

thanks to the auditors, Messrs. R. H. Davies, Friswell, and Rideal; this was seconded by Dr. P. F. Frankland, and acknowledged by Mr. Friswell.

Mr. J. Newlands proposed a vote of thanks to the Officers and Council, which was seconded by Dr. J. Voelcker, and acknowledged by Dr. Armstrong.

Professor Clowes moved that the thanks of the Fellows be tendered to the Editors, Abstractors, and Librarian for their important services during the year. Dr. Collie seconded the motion. Mr. Groves and Dr. Thorne replied.

Messrs. Foster and E. W. Voelcker having been appointed Scrutators, a ballot was taken, and as result the following were declared elected as Officers and Council for the ensuing session.

*President* : W. J. Russell, Ph.D., F.R.S.

*Vice-Presidents who have filled the office of President* : Sir F. A. Abel, C.B., D.C.L., F.R.S. ; W. Crookes, F.R.S. ; Warren de la Rue, D.C.L., F.R.S. ; E. Frankland, D.C.L., F.R.S. ; J. H. Gilbert, Ph.D., F.R.S. ; J. H. Gladstone, Ph.D., F.R.S. ; A. W. Hofmann, D.C.L., F.R.S. ; H. Müller, Ph.D., F.R.S. ; W. Odling, M.B., F.R.S. ; W. H. Perkin, Ph.D., F.R.S. ; Sir Lyon Playfair, Ph.D., K.C.B., F.R.S. ; Sir H. E. Roscoe, LL.D., F.R.S. ; A. W. Williamson, LL.D., F.R.S.

*Vice-Presidents* : G. Carey Foster, F.R.S. ; J. W. Mallet, M.D., F.R.S. ; H. McLeod, F.R.S. ; Ludwig Mond ; J. Emerson Reynolds, M.D., F.R.S. ; Robert Warington, F.R.S.

*Secretaries* : H. E. Armstrong, Ph.D., F.R.S. ; J. Millar Thomson, F.R.S.E.

*Foreign Secretary* : F. R. Japp, LL.D., F.R.S.

*Treasurer* : T. E. Thorpe, B.Sc., F.R.S.

*Ordinary Members of Council* : Norman Collie, Ph.D. ; A. H. Church, M.A. ; Frank Clowes, D.Sc. ; Wyndham R. Dunstan, M.A. ; John Ferguson, M.A. ; Charles W. Heaton ; E. Kinch ; H. F. Morley, M.A. ; F. J. M. Page, B.Sc. ; S. U. Pickering, M.A. ; R. T. Plimpton, Ph.D. ; Thomas Pardie, B.Sc.

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O B I T U A R Y   N O T I C E S .

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JAMES SMITH BRAZIER was born at Rye, Sussex, on 7th March, 1825, and losing both his parents in early childhood, he was adopted by his maternal uncle, Mr. Jeremiah Smith, of Springfield Lodge, Rye, whose name appears as one of the early promoters of the Royal College of Chemistry. To the newly-founded institution in Oxford Street, Mr. Brazier repaired in 1847, shortly after completing his school education at King William's College, Isle of Man, taking up his residence with Mr. William Johnson, who was then the Secretary; from him he gained that practical knowledge of electrotyping which often served him as a recreation, and with whom incidentally he succeeded in effecting the electro-deposition of nickel, using for this purpose the comparatively insoluble and easily purified potassium nickel sulphate.

Whilst a student at the Royal College of Chemistry, he published two papers conjointly with Dr. J. E. Mayer, the first entitled "Analyses of the Mineral Constituents of the Flax Plant, and of the Soils upon which the Plants had been Grown," read before this Society, February 5th, 1849; the second, "An Analysis of Plate Glass," was read May 21st, 1849; and in the following year, conjointly with Mr. G. Gossleth, a student from Trieste, "Contributions towards the History of Caproic and Oenanthylic Acids" was read, June 17th, 1850. Mr. Brazier was now appointed Assistant at the College, and in this capacity worked with Dr. A. W. Hofmann through part of his "Researches on the Organic Bases. IX.—Their Molecular Constitution," read before the Royal Society, April 3rd, 1851, in which paper, Dr. Hofmann, acknowledging services rendered, speaks of Mr. Brazier's experimental skill and knowledge in the highest terms of praise.\*

Leaving London, he worked for a short time with Professor T. Andrews, of Queen's College, Belfast; and from Ireland he went to Aberdeen, becoming Assistant to Dr. Thomas Clark and Dr. Andrew Fyfe successively, until, by the union of the Colleges and death of the last-named Professor (in 1861), Brazier was chosen by the University Court to succeed to the vacant Chair of Chemistry, with which he afterwards combined the duties of Secretary of the Medical Faculty, and eventually became Dean.

For more than a quarter of a century, Professor Brazier did his work at Aberdeen in a manner which cannot fail to leave a lasting

\* See R.C.C. Reports, vol. ii, p. 228.

record, training numerous students and gaining as many friends, until by illness—failure of the heart's action—he was forced to retire last autumn, and died on the 14th January in the present year, aged 64. He left a widow and five children, the three sons being in the service of the Chinese Government.

Professor Brazier was a Fellow of the Institute of Chemistry, and Vice-President of the British Association during the meeting at Aberdeen. He was frequently consulted by the Town Council, acting with Mr. John Pattinson in investigating the causes of failure of the Graving Dock, and tendering a report in 1887. He held no University degree, but arrangements had been made to confer upon him the honorary LL.D. of Aberdeen, when death intervened to prevent its fulfilment.

JOSEPH JAMES COLEMAN was the son of a pharmaceutical chemist in Lincolnshire, and was born there in 1838. His father having died when he was only ten years of age, he had no guide in his early life and studies, but, being of an industrious and studious nature, he made excellent progress in the classes of the Mechanics' Institution of Halifax, where he became connected with a business similar to his father's. He devoted all his spare time to chemistry and physics, with such success that at the early age of twenty-one he read two papers at the Chemical Section of the British Association on certain relations between the atomic weights and volumes of the elements, one of which was duly published in the Proceedings of the Association. His liking for these studies impelled him to devote himself entirely to them, and he soon abandoned his ordinary calling to become a teacher of science, an office which he filled in three different Institutions, one of which was the celebrated training college at Chester, of which the Rev. Dr. Begg was then Principal. At this time the distillation of the Boghead coal for oils and paraffin had been established on a firm footing, in Scotland, by the late Mr. James Young, F.R.S., of Kelly; and a material having been found near Chester which yielded similar products in quantity, Mr. Coleman left Chester to erect and manage works for its treatment. He was not long allowed to remain there, however, as Young's Company coveted his services, and soon secured him for the post of chemical engineer at their Bathgate works, in Scotland, where he was understood to devote himself to the investigation of the waste products with a view to economy. This he did with marked success, and, among other similar things, devised means of liquefying the so-called "incondensable gases," obtaining from them liquid products of high solvent power for many substances. The working out of this investigation led to a much more extended one, the result of which was the production of refrigerating machinery of a



valuable and unique character, with which his name will ever be associated. The "Bell-Coleman" mode of refrigeration has been one of the greatest successes of the present century, and by its means cargoes innumerable of dead meat have been brought home, in perfect condition, from all parts of the world. He contributed numerous papers to various societies and science journals, including the Royal Society of Edinburgh, the Institution of Civil Engineers, the Institution of Engineers and Shipbuilders in Scotland, the Philosophical Magazine, and the Philosophical Society of Glasgow, of which he was a member for about twenty years. For some years previous to his death, the very delicate state of his health debarred him from doing the amount of scientific work which he longed to do; indeed, his complaint, which was chronic bronchitis, compelled him to live a somewhat retired life, and he frequently expressed his regret at being unable to attend the meetings of the Glasgow and Scottish Section of the Society of Chemical Industry, of which he was Chairman. He was unmarried; and latterly he spent his time between his conservatory and his laboratory adjoining, which was fitted and equipped in a manner worthy of him and his work.

Clear-headed, warm-hearted, and with a devotedness to science which might be a rebuke to many of its followers who are more favoured in health, he fought on when many a brave man would have given himself up to the care of his complaint. He died at his residence, Bearsden, near Glasgow, on the 18th of December last, equally beloved and respected by all who knew him.

H. DEBRAY began his scientific career as Assistant to Deville at the École Normale, and aided that investigator in carrying out various researches, amongst which may be mentioned the classical work in which Deville laid the foundation of the aluminium industry. A year later, in 1859, there appeared the first of the long series of memoirs in which the names of Deville and Debray are associated. It was an investigation of the platinum metals, a subject to which the two chemists frequently returned, and the knowledge of which they did so much to extend. It may be said that the present metallurgy of platinum was created by them.

M. Debray will, perhaps, be best remembered by his work on dissociation. Deville had investigated the phenomena of dissociation, and had pointed out on what conditions they depended. But the work still lacked the requisite exact and quantitative confirmation, and it was to the task of supplying this want that M. Debray, who was, in the best sense of the word, a disciple of Deville, and had imbibed to the full his master's ideas, set himself. He selected for study classes of compounds in which the conditions of dissociation

were simple, and the amount of dissociation admitted of accurate measurement. The results, as embodied in his work "On the Dissociation of Calcium Carbonate and of Hydrated Salts," and his "Measurements of the Tensions of Dissociation," are too well known to require description here.

Among his other work may be mentioned his researches on glucinum, molybdenum, and tungsten, with the determination of the vapour-densities of the chlorides of tungsten, and his various syntheses of crystallised minerals.

On Deville's death, in 1881, M. Debray succeeded to his Chair in the École Normale, a post which he filled until his death, which took place at Paris on July 19th, 1888.

He was elected a Member of the French Academy of Sciences in 1877, and a Foreign Member of the Chemical Society in 1883.

W. F. DONKIN was the eldest son of the late Savilian Professor of Astronomy at Oxford. Born in 1845, he went at an early age to Eton, where he was educated, and where he obtained distinction in natural science. On leaving, he read for a Demyship in that subject at Magdalen College, Oxford, and was elected in 1865. Taking his degree with honours in 1868, he prosecuted his favourite study of chemistry, and became Assistant Demonstrator in the University Laboratory, besides undertaking other duties, such as those of Public Analyst to the County. He also became Science Tutor of Keble College. He married in 1876, but lost his wife the following year. This grief led him before long to think of leaving Oxford, and when, in the course of a year or two, the Professorship of Chemistry in St. George's Hospital became vacant, and was offered to him, he accepted the post, and came to live near London. To the study of chemistry he now began to add that of electricity, in which he speedily became proficient—especially in the direction of electric lighting; here, his beautiful dexterity of manipulation stood him in good stead, and he acted for some time as scientific experimenter to a well-known electrical firm, by whom his opinion was much valued. Indeed, in the opinion of one well qualified to judge, he was rapidly making his mark as a leader in experimental investigations requiring high chemical and electrical knowledge.

His marked liking for scientific pursuits was early shown; thus, when about 10 years old, and when on account of his father's health a winter had to be passed in Madeira, he made a collection of the beetles of that island, and, again, a year or two later, he collected, ground, and polished a number of geological specimens of the rocks at Clifton. About this time, also, he began photography, his apparatus consisting of a little wooden box made by the village carpenter which

served as camera, and a common magnifying glass in a pill-box for lens. With this humble outfit he produced some very respectable photographs, and it was not long before his perseverance attracted the attention of a friend who made him a present of a camera and lens, with which he made further and rapid progress. What his ultimate attainments in photography were, especially in Alpine photography, it is scarcely necessary to say. The Exhibition of his Alpine and Caucasian Photographs, which was lately open at the Gainsborough Gallery, was probably unique, for few men, if any, joined, as he did, great powers as a mountaineer to great skill in photography.

Besides making a name for himself as scientist and climber, Mr. Donkin was also an excellent musician, having inherited the talent from his father. Many may still recollect the family quartetts in which he played the viola. His steadiness and experience was such as to make him a useful addition to a performance even when professional artists of the highest rank were playing, and of late years he took on several occasions the viola part in quartetts and quintetts led by Joachim. He also did much towards furthering the cause of music in the people's concerts in the East End, and was always ready, at whatever inconvenience to himself, to help where his aid was asked.

In 1884, Mr. Donkin became Honorary Secretary of the Photographic Society, and in 1885 of the Alpine Club. In 1886, he went to the Caucasus with Mr. C. T. Dent, now the President of the Alpine Club, and last year he made a second expedition there, taking as companion Mr. H. Fox, and Mr. Dent again accompanying him. Mr. Dent was compelled to return through illness, and Mr. Donkin and Mr. Fox with their two Swiss guides continued their mountaineering. On the morning of the 29th or 30th of August, the party started to cross a glacier pass at the eastern base of the great peak marked on the Russian map as Dychtan, with the intention of bivouacking beyond the pass, and attempting the peak next day by its south-eastern face. They were never seen again, and it is probable that some disaster must have overtaken the travellers and their guides in the attempt on Dychtan. Few men have been more widely mourned than Mr. Donkin; his modesty, unselfishness, and fine character endeared him to all with whom he came in contact, and his death has caused a blank in many quarters which it will not be easy to fill.

HENRY W. FIELD, a son of John Field (an officer of the Royal Mint), was born 23rd March, 1803. His early training was in London, and also under a clergyman in Warwickshire.

In 1818, at the early age of 15, he received an appointment by Sir James Morrison as an extra clerk in the Royal Mint. In 1835, he began to study chemistry at Guy's Hospital under Aikin and Barry, and then assisted as an amateur in the Queen's Assay Office under Mr. Robert Bingley, also in the Master's Assay Office under Mr. Beckwith.

In 1850 and 1851, great changes were made in the Mint in all the departments, Mr. H. Bingley resigning, and the Master's Assay Office being abolished; the work of that department was then divided between Professor W. A. Miller and Professor Graham, under the title of "Non-resident Assayers."

The Queen's Assay Office continued to carry on its work, and Mr. Field was appointed by the Master, Sir John Herschel, to succeed Mr. Bingley, with the title of "Chief Assayer," and in this position he continued for 20 years, viz., until his resignation in 1871.

During Mr. Field's connection with the Royal Mint, he had fulfilled a career of increasing usefulness to the country for a period of more than 51 years, and during four reigns, namely, part of George III, that of George IV, William IV, and Victoria.

He died at Brighton in June, 1888, at the age of 85.

Dr. DAVID S. PRICE, superintendent of the Technological Museum at the Crystal Palace, died at Margate, after a protracted illness, on Monday, August 6th, 1888. He was the son of the late Dr. Price, of Margate, and was well known as a practical chemist. His researches on aniline dyes and in other branches of chemical manufacture, have led to important results; he was also the inventor of the very durable pavement now laid down on the roadway of London Bridge, besides having been concerned in many other prominent works. He was a Fellow of the Institute of Chemistry, and was the author of a number of papers on chemical subjects. Dr. Price's long connection with the Crystal Palace made him a well-known figure there; the Technological Museum at that place was due to his energy.

JOSEPH DENHAM SMITH was born in London in the year 1817, and died at his residence, Fair Lawn, Combe Wood, Kingston-on-Thames, December 11th, 1888.

Inheriting from his father great perseverance and shrewdness of character, and endowed with rare intellectual gifts, he was, as a young man, a careful student and a great reader, and afterwards, from his large acquaintance with English literature, a master of the English language.

Early in life, he decided on making chemistry and its allied

sciences his special work, and with the great patience he brought to bear on every subject, he was singularly fitted for work of this kind, which necessarily demands care and thoughtfulness.

In 1833, he entered the laboratory of Mr. Richard Phillips, F.R.S., one of the leading chemists of that day, and one of the first Presidents of our Society. Mr. Phillips was selected by the London College of Physicians in 1836 to revise the *Pharmacopœia Londinensis*, and it was at that time that Mr. Denham Smith acquired the knowledge of Mr. Phillips's scientific views and methods of investigation which enabled him in 1851 so satisfactorily to edit and superintend in its passage through the press Mr. Phillips's translation of the *Pharmacopœia* of that year, which the author did not live to complete.

At this time also, Mr. Smith began to contribute various papers and reviews to the Medical Journal, Philosophical Magazine, and Chemical Gazette, of which the following, published between 1835 and 1852, may be mentioned:—"On the Composition of Iodide of Iron," "On the Analysis of German Silver and the Separation of Zinc from Nickel," "On the Separation of Barytes and Strontia," "On the Composition of the Carbonate of Zinc," "On the Hydrates of Barytes and Strontia," "On the Detection and Estimation of Colophony when Dissolved in Fixed Oils," "On the alleged Conversion of Carbon into Silicon," "On the Constitution of Sub-sulphates of Copper," "On the Composition of an Acid Oxide of Iron," "On the Composition of South American Guanos, with mode of Estimating Ammonia and process for Separating Lime and Magnesia when in combination with Phosphoric Acid," "On Early Egyptian Chemistry," "Separation of Cobalt and Nickel;" and in later years Mr. Smith published various papers conjointly with his partner, Mr. Teschemacher, and his nephew, Mr. Russell Smith, on the analyses of many of the minerals and drugs met with in commerce.

From the laboratory of Mr. Phillips, the subject of our memoir went to superintend the working out of various special processes at some of the largest chemical works in the country, and for some years had the entire management of the Iron Smelting Works at Workington.

Having by this time acquired a wide knowledge of chemistry, both scientific and manufacturing, he was asked in 1852, and consented, to enter into partnership, at Highbury, with his friend, Mr. E. F. Teschemacher, the elder, who was the earliest professional analyst in London, indeed in the kingdom; and on the death of Mr. Teschemacher in 1862, Mr. Denham Smith became the senior member of the firm of "E. F. Teschemacher and J. Denham Smith," first with Mr. E. F. Teschemacher the younger, and then with his nephew, Mr. H. Russell Smith, until the day of his death.

His scientific attainments, his practical knowledge of manufacturing chemistry and metallurgy, rendered his professional opinion and assistance highly valued and widely sought after by many of the leading merchants and manufacturers in this country.

Mr. Denham Smith was one of the original members of the Chemical Society on its formation in 1841, and there now survive him six others of those constituting the Society in that year.

On December 11th, 1888, he died, after a long and trying illness, borne with patience and calmness.

Mr. JOSEPH STOREY was the youngest son of the late Mr. Isaac Storey, and was born at Bardsea, near Ulverstone, in the year 1833. His father afterwards removed to Lancaster, where he carried on a successful private school until his death at a comparatively early age.

Having received the ordinary school education, Mr. Joseph Storey entered the employment of the large firm of table baize manufacturers carried on by his elder brothers in Lancaster. After some time spent in this occupation, Mr. Storey went abroad, and on his return to England he entered as a student at Owens College, Manchester. There he passed two years, working principally at chemistry under Professor E. Frankland.

After the completion of his chemical studies, Mr. Storey settled in Lancaster, where he became engaged as consulting chemist to the firm of his brothers, and manager of certain branches of their manufacture, in which his chemical and technical knowledge was of great service.

While continuing this employment, his energy found an additional scope in the establishment of a chemical works on his own account; where he manufactured a number of miscellaneous articles, but more especially colours produced from picric acid and other derivatives of phenol. The early age in which he became engrossed in the practical application of chemistry had not enabled him to keep up with the more recondite developments of the science; but he had great experimental skill and aptitude, and was fertile in resources for encountering and overcoming manufacturing and technical difficulties.

For the latter part of his life, Mr. Storey had to contend with increasing ill health, and he died in the spring of 1888, to the grief not only of his own immediate family circle, but to that of the large number of friends to whom he was endeared for his frank and genial character.

WILLIAM WALLACE was born in Edinburgh in the year 1832. He was the son of an artist of celebrity, who survived to see him well

advanced in the study of chemistry, a profession which he had chosen in preference to his father's. His early education was acquired in Glasgow, however, to which city his family had removed when he was but eight years of age. For a considerable portion of his early life, he was a pupil at the High School of Glasgow, where, under the training of Messrs. Connell, Woolski, and other masters of note, he distinguished himself by his receptiveness and industry. At the age of 15, he began to attend the evening popular courses of chemistry given by the late Dr. Frederick Penny at Anderson's College, Glasgow, and was so captivated by what he heard and saw that he resolved to devote himself to the subject, and with that object became a regular student in that laboratory, where for several years he laboured with great assiduity, his material ability and skill in improving apparatus and methods commanding the esteem of all who knew him, while his gentlemindedness won for him many friends. With the object of extending his knowledge of organic chemistry, he then went to Liebig's laboratory at Giessen, where he remained for two years, and took the usual degree; and there can be no doubt that the great master's style influenced all his teaching and practice throughout his after life. On returning to Scotland, he became Laboratory Assistant to Dr. Penny, a post which he held for many years, and when this eminent lecturer's health failed he carried on his lectures. About the year 1856, he began business in Glasgow as an analytical and consulting chemist, and from the first it was manifest that success would attend this effort, a result due to his rare combination of perseverance, firmness, and a keen perception of the practical bearings of all his work. Already he had devoted much time to the technology of "coal-gas" and of sugar refining, subjects on which, as well as in sewage matters and questions relating to water supply, he was justly regarded as a high authority. In the year 1870, he associated himself in business with Mr. R. R. Tatlock and Dr. John Clark, and the partnership, one of the most successful of the kind in the country, was carried on for about 18 years. About the same time he was appointed Gas Examiner to the City of Glasgow, and four years later one of the Public Analysts for that city, offices which, with numerous public appointments, he retained till his death, which took place on the 5th November, 1888, at the too early age of 56. For two or three years previous to his decease, he suffered from declining health, but his keen sense of duty debarred him from taking the rest his complaint required, and he was able to attend to his business with comparatively little interruption until within a month of his decease. He was for more than a quarter of a century a Fellow of the Royal Society of Edinburgh and of the Chemical Society, and his contributions to various branches of applied chemistry and kindred

subjects were both numerous and valuable. The following are the more important of these :—

“On the Chemistry of Sugar Refining, with special reference to Smear.” “On Animal Charcoal, particularly in relation to its use for Sugar Refining.” “On the Chemistry of Sugar Manufacture and Sugar Refining.” “On the Chemistry of Sugar Refining.” “On the Bone Charcoal of Sugar Refiners.” “On the Economical Combustion of Coal-gas.” “On the Bunsen Burner.” “On the Heating Power of Coal-gas of different qualities.” “On the Composition of a peculiar Water.” “On the Conditions in which Sulphur exists in Coal.” “On the Chemistry of Sewage Precipitation.” “On the Decay of Building Stones.” “On the Decline in the Use of Coffee.” “On some peculiar Specimens of Pig Iron.”

Dr. Wallace was a member of the Philosophical Society of Glasgow for 34 years, and filled the office of President for three years, beginning 1882. At a meeting of that Society held 9th January last, a memoir relating to his life and work was read by the Secretary, Mr. John Mayer, F.C.S., and authorised for publication in Vol. XX of that Society's Proceedings, and which through the kindness of the Secretary has been consulted in preparing this note.

JOHN WILLIAMS was born in London on the 9th of March, 1824. His father was for many years Secretary of the Royal Astronomical Society, and a prominent member of other learned bodies.

As a youth, the subject of our notice entered the service of the late Mr. Thomas Morson, of Southampton Row, and while there attended the courses of instruction given in the then newly established School of Pharmacy of the Pharmaceutical Society, Fownes being the Professor of Chemistry. Having passed the necessary examinations, he became a pharmaceutical chemist, and, in due course, a member of the Pharmaceutical Society.

In 1849, he associated himself with Mr. W. King Hopkin to establish the firm of Hopkin and Williams, and Mr. Williams being a sound chemist, the firm soon gained a reputation for fine chemicals and chemically pure preparations.

Mr. Williams took considerable interest in the educational and scientific work of the Pharmaceutical Society, was for many years a member of its Council, and filled the offices both of Treasurer and President. In 1883, he was President of the British Pharmaceutical Conference, and at the time of his death, a Vice-President of the Society of Chemical Industry. He was also for a time a member of Council of the Chemical Society, and one of the original Fellows of the Institute of Chemistry. Mr. Williams read many papers on chemical subjects before the Pharmaceutical Society, Pharmaceutical



Conference, and the Chemical Society, and was always generous in giving practical advice, and, when necessary, pure specimens of chemical substances to scientific chemists engaged in original investigations.

Mr. Williams had been in failing health for several years, and retired from business about a year ago. He died, at his residence in Warwick Gardens, on the 3rd of March, 1889, within a few days of his sixty-fifth year, and was buried in Highgate Cemetery.

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XXXIII.—*Contributions to our Knowledge of the Isothiocyanates.*

By AUGUSTUS E. DIXON, M.D., Assistant Lecturer in Chemistry,  
Trinity College, University of Dublin.

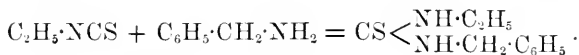
OUR knowledge of the benzylated derivatives of thiocarbamide is very limited, and I therefore considered it desirable to prepare a few of these compounds, in order to examine their chief properties, and to fill in some of the vacant places in the series. Accordingly the first two compounds described in this paper are the symmetrical dialkyl thiocarbamides, *benzylethyl-* and *benzylphenyl-thiocarbamide*.

The next three compounds (*ethylphenylsemithiocarbazide*, *acetylphenylsemithiocarbazide*, and *benzoylphenylsemithiocarbazide*) are hydrazine-derivatives. Their preparation was undertaken partly in order to ascertain whether the reaction between the thiocarbimides and hydrazines is a general one, and partly in order to compare the properties of the ethylphenylsemithiocarbazide with those of a metameric compound obtained and described by Fischer.

Further, all the compounds containing acid radicles were incidentally produced during an investigation into the chemistry of the thiocarbimides derived from the acid radicles of acetic and benzoic acids. The substances thus obtained and described in detail later on are the *acetylphenyl-* and *benzoylphenyl-semithiocarbazides* already mentioned, *acetylorthotolylthiocarbamide*, and *benzoylethylphenylthiocarbamide*, a tertiary derivative of thiocarbamide.

I. *Ethylbenzylthiocarbamide.*

Ethylthiocarbimide and benzylamine in molecular proportion were separately dissolved in alcohol. On mixing the solutions, much heat was evolved; and on evaporating the alcohol at a gentle heat a mass of white crystals was obtained, consisting of *ethylbenzylthiocarbamide*—



The yield is practically quantitative.

When recrystallised from dilute alcohol, the substance forms long, white, shining needles melting at 102–103°.

Analytical data:—

0.2201 gram, burnt with CuO and copper gauze in front, gave 27.4 c.c. nitrogen at 14.5° and 759 mm,

Or, N = 14.51 per cent.

0.3030 gram evaporated to dryness with NaOH in a nickel crucible and fused with  $\text{KNO}_3$  gave 0.3610 gram  $\text{BaSO}_4$ ,

Or, S = 16.38 per cent.

	Calculated for $\text{C}_{10}\text{H}_{14}\text{N}_2\text{S}$ .	Experiment.
N .....	14.46	14.51
S .....	16.51	16.38

Ethylbenzylthiocarbamide is slightly soluble in boiling water, and separates on cooling as an oily liquid, which soon solidifies to octahedral crystals. It is easily soluble in alcohol, ether, and chloroform, moderately soluble in benzene, and sparingly in carbon disulphide.

Ammoniacal nitrate of silver produces instantly, in the cold, a black precipitate of silver sulphide; but it is remarkable that the substance is not desulphurised in either aqueous or alcoholic solution by boiling with alkaline lead tartrate. The boiling alcoholic solution is gradually desulphurised by yellow oxide of mercury, but the product (a solid substance, which consists, presumably, of either ethylbenzylthiocarbamide or a cyanamide) has not yet been obtained in a sufficiently pure state for analysis.

## II. *Phenylbenzylthiocarbamide.*

Pure benzylamine was dissolved in about half its volume of alcohol, and to the solution was added an alcoholic solution of phenylthiocarbimide in the proportion demanded by the equation—



Much heat was developed, and fine rhombic crystals almost immediately began to separate, some floating on the surface, and rapidly growing to a considerable size. These crystals are pure white, with a greasy lustre, and closely resemble thiocarbamide in appearance. The yield of crude substance amounted to 94 per cent. of the theoretical. On recrystallisation from alcohol, in which it is moderately soluble, *phenylbenzylthiocarbamide* came down in shining, white, short, thick prisms, melting at  $153\text{--}154^\circ$ .

A sulphur determination gave the following result:—

0.2409 gram treated with NaOH and  $\text{KNO}_3$  gave 0.2263 gram  $\text{BaSO}_4$ ,

Or, S = 12.91 per cent.

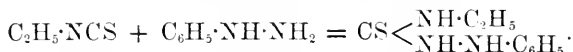
Calculated for  $\text{C}_{14}\text{H}_{14}\text{N}_2\text{S}$ , S = 13.23 „

The substance is insoluble in water, soluble in alcohol and ether, and sparingly soluble in carbon disulphide. Ammoniacal nitrate of silver

gives immediately a black precipitate in the cold, whilst the solution is readily desulphurised by boiling with alkaline lead tartrate, with formation of a speculum on the sides of the tube.

### III. *Ethylphenylsemithiocarbazide.*

Alcoholic solutions of ethylthiocarbimide and phenylhydrazine were mixed in quantities demanded by the equation—



The mixture was gently warmed until the pungent odour of ethylthiocarbimide had almost disappeared. On cooling, crystals separated. These, after being collected and pressed, formed a caroty-red mass, which on washing with alcohol became nearly white. The crystals change colour rapidly in the air, becoming first red and then greenish-blue. The crude product was dissolved in boiling alcohol, in which it is very freely soluble. On cooling, beautiful tufts of vitreous prisms separated, forming a network which penetrated the whole mass of liquid. After one or two more recrystallisations from alcohol, the substance was found to be sufficiently pure for analysis. Melting point  $121-122^\circ$  without decomposition.

Analytical data:—

0.2353 gram treated with NaOH and  $\text{KNO}_3$  gave 0.2736 gram  $\text{BaSO}_4$ ,

Or, S = 15.98 per cent.

0.1825 gram, burnt with CuO and copper gauze in front, gave 33.2 c.c. nitrogen at  $11^\circ$  and 763 mm.,

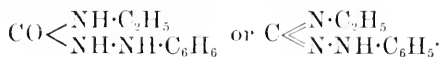
Or, N = 21.76 per cent.

	Calculated for $\text{C}_9\text{H}_{13}\text{N}_3\text{S}$ .	Experiment.
N .....	21.58	21.76
S .....	16.42	15.98

*Ethylphenylsemithiocarbazide* when pure is not discoloured by exposure to air; it is almost insoluble in water, very easily soluble in hot alcohol, moderately in cold, soluble also in ether and chloroform. The solution in alcohol or warm water gives, on addition of a few drops of ferric chloride solution, a blood-red colour, changing rapidly to a deep blackish-green; this reaction is very delicate. Copper sulphate produces a bright grass-green colour, which is destroyed by ammonia, with production of a black precipitate. Ammoniacal nitrate of silver produces a white, curdy precipitate, which is decomposed

on boiling, while a brilliant mirror of silver sulphide separates out on the sides of the tube.

The melting point, as already stated, is between  $121^{\circ}$  and  $122^{\circ}$ ; it is worthy of note that a metameric compound,  $\text{CS} < \begin{smallmatrix} \text{NH} \cdot \text{C}_6\text{H}_5 \\ \text{NH} \cdot \text{NH} \cdot \text{C}_2\text{H}_5 \end{smallmatrix}$ , obtained by Fischer from phenylthiocarbimide and ethylhydrazine (*Ann.*, 199, 296), is recorded as melting at  $109-110^{\circ}$ . An attempt was made, by treating the warm alcoholic solution with mercuric oxide, to obtain a desulphurisation-product, either—



The desulphurisation is readily effected, but the decomposition proceeds further, and effervescence takes place with evolution of gas containing carbon oxysulphide.

#### IV. *Acetylphenylsemithiocarbazide.*

Acetylthiocarbimide and phenylhydrazine in molecular proportion, each dissolved in pure anhydrous benzene, were mixed together. So much heat was evolved that the liquid at once began to boil freely, and in a few moments a sticky mass of brown, oily droplets fell to the bottom of the flask, which mass slowly deposited crystalline matter, and as the benzene evaporated, a further quantity of solid matter separated. The whole was drained on the filter-pump, the residue pressed between folds of bibulous paper, and recrystallised from hot benzene. The product was washed with benzene, dried, and again recrystallised from boiling alcohol. Thus was obtained a small quantity of short, thick, white prisms, melting at  $178-179^{\circ}$  without decomposition. The yield is very small.

A sulphur determination gave the following result:—

0.2993 gram, treated with NaOH and  $\text{KNO}_3$ , yielded 0.3346 gram  $\text{BaSO}_4$ ,

Or, S = 15.36 per cent.

Calculated for  $\text{C}_9\text{H}_{11}\text{N}_3\text{SO}$ , S = 15.47 „

The reaction may be represented thus:—



Ammoniacal silver nitrate solution gives a bulky, white precipitate, which slowly darkens on boiling. The substance is scarcely desulphurised even on continued boiling with alkaline lead solution.

V. *Benzoylphenylsemithiocarbazide.*

Benzoylthiocarbimide and phenylhydrazine in molecular proportion, both largely diluted with anhydrous ether, were gradually mixed, the flask being cooled by immersion in water. The substances combined with violent—almost explosive—action, and solid matter separated out till the liquid became pulpy. The pulpy mass was drained, pressed, and recrystallised twice from boiling alcohol, in which it is somewhat sparingly soluble. Thus purified the substance forms tangled wisps of pure white, silky needles, resembling asbestos in appearance. It does not melt at  $220^{\circ}$ , and fails to reduce alkaline lead solution, even on prolonged boiling.

Analytical data:—

0.3060 gram, treated with NaOH and  $\text{KNO}_3$ , gave 0.2600 gram  $\text{BaSO}_4$ ,

Or, S = 11.68 per cent.

0.2225 gram, burnt with CuO and copper gauze in front, gave 29.6 c.c. nitrogen at 13 C. and 768.5 mm.

Or, N = 15.89 per cent.

	Calculated for $\text{C}_{13}\text{H}_{13}\text{N}_3\text{SO}$ .	Experiment.
N .....	15.53	15.89
S .....	11.82	11.68

The following equation represents the interaction:—

VI. *Acetylorthotolylthiocarbamide.*

Acetylthiocarbimide was added, drop by drop, to a solution of orthotoluidine in anhydrous alcohol. Energetic action took place, and solid matter separated, which was collected, dried with bibulous paper, and dissolved in boiling alcohol. On cooling, brilliant prisms separated, pale lemon-yellow in colour, and melting without decomposition at  $184^{\circ}$ .

Analytical data:—

0.6400 gram, on treatment with NaOH and  $\text{KNO}_3$ , gave 0.7466 gram  $\text{BaSO}_4$ ,

Or, S = 16.03 per cent.

0.2375 gram, burnt with CuO and copper gauze in front, gave 27 c.c. nitrogen at  $10^{\circ}$  C. and 759 mm.

Or, N = 13.59 per cent.

	Calculated for $C_{10}H_{12}N_2SO$ .	Experiment.
N .....	13.48	13.59
S .....	16.68	16.03

The reaction is expressed thus:—



The substance is insoluble in water, soluble in alcohol. Silver nitrate produces immediately, in the cold, a black precipitate, and the solution is also readily desulphurised by boiling with alkaline lead tartrate.

#### VII. *Benzoylphenylethylthiocarbamide.*

Benzoylthiocarbimide was added to ethylaniline diluted with a little ether. Heat was evolved, and, on cooling, the mixture solidified to a pasty mass of yellow crystals. These were drained, pressed, and recrystallised twice from alcohol, from which the substance separates in well-formed, pale lemon-yellow prisms, melting with decomposition at 133—134°.

Analytical results:—

0.2069 gram, burnt with CuO and copper gauze in front, gave 17.3 c.c. nitrogen at 12° C. and 764 mm.

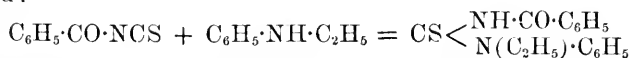
Or, N = 9.97 per cent.

0.2041 gram, treated with NaOH and KNO<sub>3</sub>, gave 0.1780 gram BaSO<sub>4</sub>,

Or, S = 11.98 per cent.

	Calculated for $C_{16}H_{16}N_2SO$ .	Experiment.
N .....	9.88	9.97
S .....	11.23	11.98

Thus the expected trisubstituted thiocarbamide has been produced:—



The substance is insoluble in water, soluble in alcohol and ether. Like other trisubstituted thiocarbamides, it shows itself very stable towards chemical reagents. With alcoholic silver nitrate, a white precipitate is formed, soluble on warming, and coming down again as the solution cools; this precipitate is not blackened by ammonia, even on continued boiling. Neither is the solution in alcohol desulphurised by boiling with alkaline solution of lead.

*Chemical Laboratory,  
University of Dublin.*

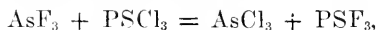
## XXXIV.—On Thiophosphoryl Fluoride.

By T. E. THORPE, F.R.S., and J. W. RODGER, Associate of the Normal School of Science, S. Kensington.

IN a short paper bearing the above title, published in the Transactions of the Society during the summer vacation of last year (Trans., 1888, **53**, 766), we announced the existence of a new gaseous substance of the formula  $\text{PSF}_3$ , to which we gave the name of *thiophosphoryl fluoride*. The present communication contains the results of the experiments which have served to establish the nature and composition of the new compound.

Arsenic trifluoride acts with great violence on phosphorus pentachloride, with the formation of phosphorus pentafluoride and arsenic trichloride (Thorpe, *Proc. Roy. Soc.*, **25**, 122). Phosphorus trichloride mixes with arsenic trifluoride, and on gently warming, the mixture evolves the gaseous phosphorus trifluoride (Moissan, *Ann. Chim. Phys.* [6], **6**, 433).

The behaviour of thiophosphoryl chloride with arsenic trifluoride is however very different. If arsenic trifluoride is dropped into phosphorus thiochloride in the cold, or if a mixture of the two compounds is boiled under ordinary pressures, no action takes place. When, however, the mixture is heated in a sealed glass tube at  $150^\circ$ , arsenious sulphide separates, and on cooling and opening the tube considerable quantities of gas are evolved. The nature of the gaseous product varies with the relative proportions of the arsenic fluoride and phosphorus thiochloride. If the reacting substances are heated in the proportions demanded by the equation—

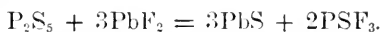


analysis shows that about  $\frac{1}{6}$ th of the gas produced consists of thiophosphoryl fluoride, the remainder being made up of the fluorides of phosphorus and silicon. As the amount of the thiophosphoryl chloride is increased relatively to that of the arsenic fluoride, larger proportions of phosphorus thiofluoride are produced, until when four equivalents of thiophosphoryl chloride are used to one equivalent of arsenic fluoride, the gas evolved is *spontaneously inflammable*, and exhibits in general the characteristic features of the pure thiophosphoryl fluoride. It was found impossible, however, to entirely prevent the formation of silicon tetrafluoride and phosphorus trifluoride by this means, and although our subsequent experience with the gas has enabled us to devise a method for separating these



compounds from thiophosphoryl fluoride, it was evident from the relatively large quantity of arsenious sulphide invariably produced, that the method, even apart from the manipulative difficulties of working with sealed tubes containing gas under pressure, was neither a convenient nor an economical mode of preparing the new substance.

If arsenic trifluoride is heated with phosphorus pentasulphide in a sealed glass tube, the gas evolved consists mainly of silicon tetrafluoride. Lead fluoride, however, readily reacts, on heating it with phosphorus pentasulphide, producing thiophosphoryl fluoride in considerable quantity—



A mixture of red phosphorus, sulphur, and lead fluoride also gives rise to thiophosphoryl fluoride, but if the materials are used in the proportions required by the above equation, the reaction is extremely violent. It may, however, be moderated by using a large excess of lead fluoride. The mixture should be placed in a thin layer in a glass tube of narrow bore and which is gradually heated from behind forwards, so that the gaseous product as it is formed passes over the cold anterior portions of the tube and materials.

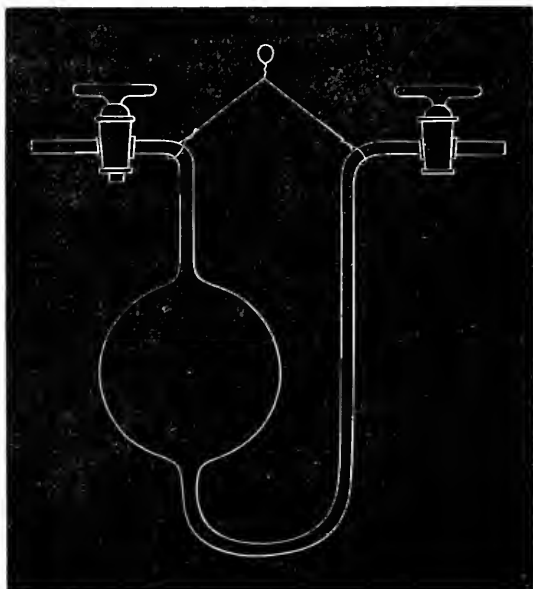
Bismuth trifluoride may be used instead of lead fluoride in the reaction, but in this case a brass tube must be employed, as the temperature at which the gas is evolved is considerably higher, and large quantities of phosphorus trifluoride are apt to be simultaneously formed.

On the whole, we found that the most convenient method is to heat a mixture of lead fluoride and phosphorus pentasulphide, but in order that the gas shall be obtained pure, certain precautions are absolutely necessary. Thiophosphoryl fluoride is readily altered by contact with air and moisture: hence it is necessary that the materials should be perfectly anhydrous, and that every trace of free oxygen should be absent. Moreover, as the gas is readily decomposed by heat, it is desirable that it should be produced at the lowest possible temperature. The best method of procedure is as follows: A quantity of freshly prepared phosphorus pentasulphide, made from washed and perfectly dry amorphous phosphorus and powdered roll sulphur, is quickly pounded with the requisite quantity of pure freshly fused lead fluoride, and the mixture is placed in a thin uniform layer in a dry leaden or "composition" tube, open at both ends. One end of the tube is fitted with a caoutchouc cork and glass delivery tube, whilst the other is attached to an apparatus yielding a supply of pure dry nitrogen. The air within the tube is rapidly swept out by the dry nitrogen, and the tube is gently heated in order to get rid of any sulphuretted hydrogen produced by the action of

atmospheric moisture on the phosphorus pentasulphide. When the tube is completely filled with nitrogen, the current of this gas is stopped and the leaden tube is heated from behind forwards by a small Bunsen flame. The reaction begins at about  $170^{\circ}$ , and as it is advisable to keep the temperature as low as possible consistent with the production of the gas, it should not exceed  $250^{\circ}$ . The gas is collected over dry mercury and may be stored in a glass gas-holder. The gas-holder should contain a few fragments of quicklime, the pores of which should be freed from air by passing small quantities of dry nitrogen into the gas-holder and repeatedly exhausting by means of the Sprengel pump. The thiophosphoryl fluoride is not allowed to pass into the holder until a sample is wholly absorbed by a dilute solution of potash or ammonia. In order to get rid of the small quantity of nitrogen adhering to the lime, as soon as two or three cubic centimetres of gas have entered the holder, the latter is connected with the Sprengel pump and the gas and nitrogen sucked out, this operation being repeated twice or thrice. The rest of the gas is passed into the holder, and after standing for a day or so over the lime, which removes the phosphorus fluoride and any traces of silicon tetrafluoride, is pure thiophosphoryl fluoride.

*Determination of Vapour-density.*—A bulb of about 240 c.c. capacity and fitted with tubes and stopcocks, as seen in Fig. 1, after being

FIG. 1.



cleaned and weighed, is placed in a bath of water and filled with dry nitrogen. The bulb is then connected with a small mercury gas-holder, containing thiophosphoryl fluoride, made and purified as above described, and the nitrogen is slowly displaced from below upwards by the thiophosphoryl fluoride. The exit-tube of the bulb is attached to a piece of glass tubing, which dips a short way under mercury, so as to cut off the direct connection with the air. The bulb is immersed in the bath nearly to the level of the stopcocks, and a current of cold water, carrying with it a stream of air-bubbles, is allowed to enter at the bottom of the bath, and flow away at an opening near the top. The stream of air-bubbles is sufficiently strong to keep the mass of the water in circulation, and thus tends to render the bath of uniform temperature. When all the gas has passed over, the cocks of the bulb are turned, the tube dipping under the mercury removed, one cock momentarily opened to equalise the pressure, and the temperature of the bath and the height of the barometer noted. The dried bulb, after standing in the balance-case for about an hour, is then re-weighed.

To determine the amount of the residual nitrogen, the entry-tube of the bulb (both stopcocks being closed) is connected by means of caoutchouc tubing with a large burette containing a dilute solution of pure caustic potash. The potash is caused to fill the caoutchouc tube and the entry-tube of the bulb up to the stopcock. The stopcock is next opened and the potash allowed to enter the bulb. The gas is slowly absorbed, the bulb being meanwhile immersed in a vessel of water at a constant temperature. When the absorption is complete and the contents of the bulb are brought to the temperature of the water, the levels of the liquid in the bulb and burette are equalised, and the burette reading taken. The burette is then raised, and the stopcock of the exit-tube of the bulb is carefully opened. The level of the potash solution within the bulb rises until it reaches the stopcock, which is then closed, when the levels are again equalised and a second reading on the burette taken. The difference between the two readings gives directly the volume of the residual nitrogen at the temperature of the bath and under the atmospheric pressure.

The details of two experiments carried out in this way are as follows:—

## I.

Capacity of bulb at 15·8° and 776 mm.....	239·86 c.c.
Weight of bulb in air at 17·1° and 771 mm...	59·7543 grams.
Weight of bulb in air at 17·0° and 771 mm. filled with gas and residual nitrogen at 10·7° and 771 mm. ....	60·3954 „
Volume of residual nitrogen at 11·3° and 771 mm.....	78·9 c.c.
Reduced weight of gas and residual nitrogen	0·9372 gram.
Weight of nitrogen .....	0·0964 „
Weight of thiophosphoryl fluoride.....	0·8408 „
Volume of gas + residual nitrogen at 0° and 760 mm.....	234·15 c.c.
Volume of residual nitrogen at 0° and 760 mm.	76·86 c.c.
Volume of thiophosphoryl fluoride .....	157·29 „
157·29 c.c. of thiophosphoryl fluoride weigh .	0·8408 gram.
1000 c.c. of thiophosphoryl fluoride weigh. ..	5·3455 „
Vapour-density ( $H = 1$ ) = 59·66.	

## II.

Capacity of bulb at 15·8° and 776 mm.....	239·86 c.c.
Weight of bulb in air at 15·6° and 778 mm...	59·7282 grams
Weight of bulb in air at 15·1 and 778 mm. filled with gas and residual nitrogen at 7·7° and 778 mm.....	60·5274 „
Volume of residual nitrogen at 9·6° and 777 mm.....	43·4 c.c.
Reduced weight of gas and residual nitrogen	1·0995 gram.
Weight of nitrogen .....	0·0538 „
Weight of thiophosphoryl fluoride .....	1·0457 „
Volume of gas + residual nitrogen at 0° and 760 mm. ....	238·81 c.c.
Volume of residual nitrogen at 0° and 760 mm.	42·86 „
	195·95 „
195·95 c.c. of thiophosphoryl fluoride weigh .	1·0457 gram
1000 c.c. of thiophosphoryl fluoride weigh. ..	5·3355 „
Vapour-density ( $H = 1$ ) = 59·56.	
The calculated vapour-density of $\text{PSF}_3$ is 60·0.	

*Analysis of Thiophosphoryl Fluoride.*—The solution of the gas in the dilute potash was transferred to a 500 c.c. measuring flask, and the bulb carefully washed out and bromine-water added to the liquid until the colour persisted after repeated shaking, when the solution was diluted to the mark. In order to determine the *sulphur*, an aliquot portion of the solution was acidified with hydrochloric acid and mixed with barium chloride and the barium sulphate weighed. To obtain the amount of *phosphorus*, a second aliquot portion of the liquid was treated with ammonium molybdate solution in the usual manner, and the precipitate converted into magnesium ammonium phosphate and weighed as pyrophosphate. The results were as follows:—

- I. One-fifth of a solution containing 0.8408 gram of gas gave 0.3223 gram barium sulphate.  
 A second fifth gave 0.1557 gram magnesium pyrophosphate.  
 II. One-fifth of a solution containing 1.0457 gram of gas gave 0.3992 gram barium sulphate.  
 A second fifth gave 0.1924 gram magnesium pyrophosphate.

	Calculated for PSF <sub>3</sub> .	Found.	
		I.	II.
Phosphorus .....	25.83	25.85	25.69
Sulphur .....	26.66	26.32	26.22
Fluorine .....	47.51	—	—
	<hr/> 100.000		

*Properties of Thiophosphoryl Fluoride.*—At ordinary temperatures thiophosphoryl fluoride is a transparent, colourless gas, which, under the application of about 10 to 11 atmospheres pressure, condenses to a colourless liquid. Neither the gas nor the liquid acts to any appreciable extent on dry glass at ordinary temperatures. In air or oxygen the gas is spontaneously inflammable, and its oxidation products have a disagreeable, irritating smell, in which that of sulphur dioxide can readily be detected. Under the action of heat or the electric spark the gas is readily decomposed, with the separation of sulphur and phosphorus and the formation of phosphorus fluorides. If the decomposition be effected in a glass tube heated to a sufficiently high temperature, the gaseous product eventually consists entirely of silicon tetrafluoride.

Thiophosphoryl fluoride has no action on mercury, oil of vitriol, carbon bisulphide, or benzene. In ether, it is soluble to some extent, and the solution burns with a greenish flame. The gas is not readily dissolved by water, and dilute solutions of potash, soda, and ammonia

dissolve it only with comparative slowness. It unites with gaseous ammonia to form a white solid, and is completely absorbed by peroxide of lead. If passed over gently heated sodium the metal takes fire, and burns with a red flame, and the residual mass in presence of water evolves spontaneously inflammable phosphuretted hydrogen.

As certain of these reactions are of considerable interest, we have studied them in detail.

*Action of Air on Thiophosphoryl Fluoride.*—In contact with air, pure thiophosphoryl fluoride is speedily decomposed, the nature of the appearances attending the decomposition varying to a great extent with the conditions under which the admixture takes place.

If a very slow stream of the pure gas be allowed to issue from a narrow platinum jet into the air, a white fume is instantly formed. No indication of flame is evident in daylight if the stream is sufficiently slow, but in the dark, the white fume is seen to be traversed in the vicinity of the jet by a blue, flickering flame. On increasing the current of the issuing gas the blue, flickering flame becomes more pronounced, and eventually travels back to the orifice of the jet, and ignites the stream. If the supply of gas is maintained, the gas continues to burn, giving off copious white fumes. The flame is greyish-green in colour, and is tipped with a faintly luminous dull yellow portion, a light-blue zone occurring close to the platinum jet.

If, instead of allowing the gas to issue from a jet, a considerable bulk be suddenly permitted to come in contact with the air, the appearance is considerably modified. When the delivery tube of an apparatus in which the gas is being generated dips beneath the surface of mercury, and is surrounded by a piece of wide glass tubing about 6 inches long, open top and bottom, and with its lower end under the mercury, the wide tube becomes gradually filled with the gas, which is prevented from combining rapidly with the oxygen of the air by a layer of decomposition products formed from the first bubbles of the gas which entered the tube. When the tube is nearly filled with the gas, which may be ascertained by noting the position of the layer of fume which roughly indicates the line of separation of the gas and air, on lifting its lower end out of the trough the gas quickly falls down on to the surface of the mercury, combination rapidly takes place, accompanied first of all by a beautiful blue flash of light followed by the greyish-green flame observed in the case of a jet of the gas. The shape of the flame indicates that the gas has spread itself for a considerable way over the surface of the mercury before combination ensues. If the layer of fume be allowed to rise above the top of the tube, the gas is no longer protected from the action of the air, and takes fire from above and burns with the greyish-green flame.

The action of air upon thiophosphoryl fluoride may be further illustrated by rapidly mixing a small quantity of the gas contained in a glass vessel with a large excess of air. For this purpose a small glass gas-holder provided with a stopcock at the top and tubulus at the bottom is filled with mercury and placed in the trough, the tubulus being open, and a few cubic centimetres of the gas are next introduced. If the cock is now opened the mercury falls, and air rapidly enters the gas-holder. White fumes are at once formed, and increase in quantity with the amount of air until, when a certain volume has been introduced, a sharp explosion takes place accompanied by light and heat, and the mercury is forcibly ejected from the cylinder.

*Action of Oxygen on Thiophosphoryl Fluoride.*—When a quantity of thiophosphoryl fluoride is passed into a confined volume of oxygen contained in a eudiometer standing over mercury, the fluoride, being about four times heavier than the oxygen, collects on the surface of the mercury, and burns quietly with a yellow flame, and a white fume is produced which quickly settles on the sides of the eudiometer. If the oxygen is passed into the gas, combination is more rapid, and a much denser deposit settles. When, however, the gas is gradually passed into the oxygen, that is, in a slow stream of small bubbles, the behaviour of the two gases is considerably altered. The first few bubbles on reaching the oxygen inflame, giving a blue flash of light. As oxidation products collect on the surface of the mercury, more bubbles may be added without any signs of combination until when a certain amount of gas has accumulated in the oxygen, a bright-yellow flash is seen to traverse the gaseous mixture, and is followed by a smart detonation. On adding more of the fluoride, a second detonation may be obtained either spontaneously or by increasing the pressure of the mixture. As a rule, a third explosion cannot be obtained either by agitating the gases or by increasing the pressure on them, even although oxygen may still be in excess. Dry oxygen and thiophosphoryl fluoride may in fact exist together in presence of a sufficient quantity of oxidation products, apparently without interaction, provided all traces of moisture are carefully excluded from the mixture. If lead fluoride is heated with phosphorus pentasulphide which has been kept in a bottle for some time, with no special pains to exclude air from the apparatus, gas is evolved which can be mixed with excess of dry oxygen without the slightest change taking place, even when the eudiometer is gently heated. The mixture, however, at once inflames on exposure to the air. That it is the moisture in the air which serves to start the reaction is proved by the fact that on passing fragments of blotting-paper moistened with water into the mixture of gas and oxygen their explosive union instantly follows.

These facts render it difficult to experimentally determine the

exact chemical nature of the action of oxygen upon the gas. We have, however, made the attempt. A measured quantity of thiophosphoryl fluoride was passed into a small graduated tube containing a known volume of dry oxygen gas (from three to five times the volume of the fluoride) standing over mercury. After combination had taken place, and it had been ascertained that all the thiophosphoryl fluoride had been oxidised, the apparatus was allowed to cool down to the temperature of the air, and the volume of the mixed gases was determined. These were then treated either by lead peroxide or by a strong solution of potash, which absorbs the products of combustion; the residual gas is pure oxygen, and its volume represents the amount which has taken no part in the reaction. The original volume of the oxygen and of the thiophosphoryl fluoride, together with the volume of the products and of the residual oxygen being known, it is easy to calculate the amount of oxygen which is required to oxidise a definite volume of the gas as well as the volume of the products formed and the contraction which has ensued.

From the mode in which the thiophosphoryl fluoride is passed into the oxygen it is difficult to introduce it in a uniform stream, but when this is effected the first bubbles of gas take fire and the rest explodes as already described; in such cases the amount of oxygen used and the amount of products formed are always greater than when the gas is passed up in quantity and burned, either entirely or in part, without explosion.

The results obtained are as follows; for the sake of simplicity the ratios only of the volumes are given:—

*Action of Oxygen on  $\text{PSF}_3$ .*

No. of expt.		Gas.	Products formed.	Oxygen used.	Contraction.
I ....	Gas has stood over lime; part burns; part explodes ....	1	1·535	1·29	0·755
II ....	Same gas as I; all burns quietly .....	1	1·433	1·143	0·7105
III ....	Gas made in "compo" tube; part burns; part explodes.	1	1·372	1·219	0·8457
IV ....	Same gas as III; all explodes	1	1·492	1·259	0·7675
Va ....	Same gas; all explodes but one little bubble.....	1	1·596	1·209	0·6126
Vb ....	Products of Va are sparked; bubble is thus combined..	1	1·444	1·209	0·7649
VI ....	Same gas. Eudiometer is heated by bunsen.....	1	1·39	1·096	0·71

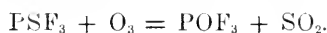
Rejecting VI, as in that case the tube was heated, and Va, as the



little bubble of gas evidently did not combine spontaneously, and only did so in passing the electric spark, *Vb*, the values are—

	Gas.	Pro- ducts.	Oxygen.	Contraction.	Gas.	Pro- ducts.	Oxygen.	Contraction.
I.....	1	1·53	1·29	0·75	4	6·14	5·16	3·05
II.....	1	1·43	1·14	0·71	4	5·73	4·57	2·84
III.....	1	1·37	1·22	0·85	4	5·49	4·88	3·38
IV.....	1	1·50	1·26	0·77	4	5·97	5·04	3·07
<i>Vb</i> .....	1	1·44	1·21	0·76	4	5·78	4·84	3·06
Mean values..	1	1·45	1·22	0·76	4	5·82	4·90	3·07
Rejecting III—								
Mean values..	1	1·475	1·225	0·747	4	5·905	4·903	3·00

These results are not very concordant, and the reason of their discrepancy will be evident from what follows. The numbers, however, at once serve to show that the reaction between thiophosphoryl fluoride and oxygen is not in accordance with the equation—

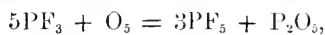


In this equation, 5 vols. of mixed gases condense to form 4 vols. of products; the contraction being one-fifth of the initial volume.

The numbers on the whole tend to show that 4 vols. of gas require 5 vols. of oxygen and give 6 vols. of gaseous products with a contraction of 3 vols., but it will be observed that certain of the experiments differ considerably from these values. What probably takes place is, that a portion of the gas is acted upon by oxygen thus:—

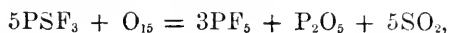


and that at the high temperature the phosphorus trifluoride is converted partly into phosphoryl fluoride and partly into phosphorus pentafluoride in the manner already indicated by Moissan:—



the ratio of these products being dependent upon the conditions under which the reaction takes place.

As phosphorus pentoxide and sulphur dioxide are unquestionably products of the action of oxygen upon the gas, the reaction in all probability tends towards the equation—



which implies that 4 vols. of the gas require 6 vols. of oxygen and

yield 6.4 vols. of products. If a portion of thiophosphoryl fluoride was decomposed only into the trifluoride and sulphur dioxide, which is highly probable, less oxygen would be needed and a less volume of combustion products would be obtained, which is exactly what is observed. It is noteworthy that in all cases in which the decomposition took place with violent explosion, that is, at a high temperature, the amount of oxygen used and the volume of combustion products formed was greatest.

On introducing a flame of thiophosphoryl fluoride burning in air into an atmosphere of oxygen, the flame becomes reduced in size and much more luminous. Its colour changes from greyish-green to bright yellow, and dense, white fumes are given off. The solution of the products formed smells strongly of sulphur dioxide, and gives the reactions of phosphoric acid.

In some respects the behaviour of thiophosphoryl fluoride with oxygen resembles that of phosphorus trifluoride as observed by Moissan. Moissan found that a strong spark was necessary to effect the union of the trifluoride with oxygen, and that in presence of an excess of oxygen, which acts as an inert gas, the explosion was not produced. When the amount of oxygen was double that necessary to produce the oxyfluoride, the two gases only combined by the prolonged action of the spark without detonation or incandescence. Moissan also found that a mixture of 1 vol. of the trifluoride with half a volume of oxygen, which detonated violently on passing a sufficiently strong electric spark, did not ignite by contact with an ordinary gas flame. The temperature was not sufficiently high to effect the combination. On bringing the oxyhydrogen flame in contact with the mixture contained in a wide tube, combustion was produced and the flame descended, but without explosion, to the bottom of the tube. These experiments show that the oxyfluoride is only produced at a relatively high temperature, and serve to strengthen the improbability that this gas is formed at all events in any large quantities during the combustion of thiophosphoryl fluoride in air or in oxygen.

Thiophosphoryl fluoride cannot be burned with safety from a jet in a closed apparatus through which a current of dry air or oxygen is passing. The flame is liable to be extinguished by a current of air or oxygen sufficiently powerful to carry over the products into the absorption-tubes. As a rule, the gas speedily relights itself, but not before sufficient unburnt gas has escaped to form a spontaneously explosive mixture. We made two attempts to burn the gas in a closed space, and in each case the apparatus was shattered by explosion.

These experiments on the behaviour of thiophosphoryl fluoride in

contact with air or oxygen are interesting as illustrating the extreme instability of the gas. Its ignition temperature is evidently very low, and a very slight alteration of the conditions under which it is presented to oxygen serves to determine whether the heat evolved by the spontaneous combination of a part of the gas suffices to ignite the remainder. On allowing a slow stream of the pure gas to issue into the air from a narrow jet, combination is seen to take place, but it is only when the current is increased that the rise of temperature is sufficient to ignite it. The cooling action of the air is sufficient to prevent any flame. Even when a considerable volume of the gas is poured out into the air, an appreciable lapse of time occurs before the temperature from the heat of combination is high enough to ignite the rest of the gas. We have on several occasions partially filled the empty space in a mercury trough with the gas without any flame resulting, but on gently blowing upon the mixture the whole has immediately ignited. Small quantities of indifferent gases greatly influence the temperature of ignition, and in some cases, as in the experiments with oxygen, entirely prevent the spontaneous oxidation of the gas. If the amounts of the diluent substances are considerable, the mixture of oxygen and thiophosphoryl fluoride may be subjected to a relatively high temperature without appreciable change. On sending an excess of the fluoride into a confined volume of air, partial combination at once ensues, but even on passing electric sparks through the mixture for some time, oxygen still exists uncombined. If the amount of the indifferent gas is small, a very slight cause will determine the explosive union of oxygen and thiophosphoryl fluoride; thus, if the mixture be shaken, or if its tension be suddenly increased, combination at once ensues with explosion. The mixture may also be detonated by bringing a drop of water into it. Gas containing a slight admixture of the products of combustion may issue into the air in a rapid stream with no appearance of flame, but if a test-tube containing warm water is held in the current it is ignited; on withdrawing the warm tube, the flame is at once extinguished, but reappears when the tube is again brought into the stream.

As might be expected from the low-ignition temperature, and from the ease with which the flame is extinguished, its temperature is very low. It is probably one of the coldest flames known. Our hands have frequently been surrounded by it without any too inconvenient sensation of heat.

*Action of Water on Thiophosphoryl Fluoride.*—If a stream of thiophosphoryl fluoride is sent through water, comparatively little of the gas is absorbed. The bubbles rise to the surface, and take fire immediately on reaching the air, forming rings of white smoke. In

order that any appreciable quantity may be dissolved, the gas must be shaken with the water for some time. The solution is acid to test-paper, smells of sulphuretted hydrogen, and gives the reactions for phosphoric and hydrofluoric acids. The decomposition is in accordance with the equation—



If the solution is effected in a vessel of flint-glass, the liquid at once becomes black, owing to the action of the hydrofluoric acid and sulphuretted hydrogen upon the lead silicate.

*Action of Alkaline Solutions upon Thiophosphoryl Fluoride.*—Thiophosphoryl fluoride is more readily dissolved by a solution of potash or soda than by water, but it is only by acting upon a confined volume of the gas, and frequently shaking the liquid, that large quantities can be absorbed.

Wurtz (*Ann. Chem. Phys.* [3], 20, 472) has shown that alkaline solutions react on thiophosphoryl chloride,  $\text{PSCl}_3$ , with the formation of a thiophosphate and a chloride. Thus with soda—



Analogy would appear to indicate that thiophosphoryl fluoride would behave in a similar manner.

Berthelot, arguing from the heat of solution of phosphorus trifluoride in alkaline solutions, has inferred the existence of a fluo-phosphoric acid. And it is, of course, possible that this compound might be formed from thiophosphoryl fluoride.

In order to ascertain the exact nature of the decomposition, a quantity of the gas was dissolved in pure soda solution, contact with glass being carefully avoided, and the solution was slowly evaporated in a large platinum dish. As crystals were formed, the mother-liquors were decanted, and the successive fractions, after being washed with a little water, were dried and analysed. The first fraction was found to consist of almost pure sodium fluoride, and the succeeding fractions contained gradually increasing quantities of sodium thiophosphate. The decomposition by alkaline solutions is strictly analogous to that of thiophosphoryl chloride as described by Wurtz:—



*Action of Ammonia on Thiophosphoryl Fluoride.*—If ammonia gas is passed into a confined volume of thiophosphoryl fluoride the two gases immediately combine, heat is evolved, and a white solid substance is formed. To determine quantitatively the volume ratios of the gases taking part in the reaction, measured quantities of dry ammonia were passed into a measured amount of thiophosphoryl fluoride and the

contraction was noted. Ammonia sufficient to condense part of the gas is added first of all, and after cooling and noting the volume more is added until all the gas has entered into combination.

The following are the numbers obtained in two consecutive trials: the volumes are reduced to standard temperature and pressure:—

Original volume of ammonia gas.....	39.07 c.c.		
„ „ thiophosphoryl fluoride.....	7.51 „		
After 1st admixture—			
Residual vol. of NH <sub>3</sub> ..	18.52 c.c.	NH <sub>3</sub> used....	20.55 c.c.
„ „ PSF <sub>3</sub> ..	2.34 „	PSF <sub>3</sub> „ ....	5.17 „
After 2nd admixture—			
Residual vol. of NH <sub>3</sub> ..	7.51 c.c.	Total NH <sub>3</sub> used	31.02 c.c.
Excess of NH <sub>3</sub> added..	0.74 „	PSF <sub>3</sub> „	7.51 „
1st admixture.....	1 vol. of PSF <sub>3</sub> condenses	3.98 vols. NH <sub>3</sub> .	
2nd „ .....	1 „ „	4.13 „	

One molecule of thiophosphoryl fluoride appears, therefore, to combine with 4 mols. of ammonia to form a solid product. In this respect its behaviour is analogous to that of thiophosphoryl chloride, PSCl<sub>3</sub>. Gladstone and Holmes (*Chem. Soc. J.*, **18**, 7) found that this substance could not absorb more than four equivalents of ammonia, and they were of opinion that the reaction was in accordance with the equation—



Schiff, on the other hand, represents the reaction on the supposition that *thiophosphotriamide*, PS(NH<sub>2</sub>)<sub>3</sub>, is formed,

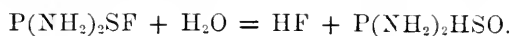


although no analytical data are given in support of this view of the action (*Ann. Chim. Pharm.*, **101**, 292).

If a reaction corresponding to Schiff's equation took place in the case of thiophosphoryl fluoride, 6 vols. of ammonia ought to be condensed. The volume ratios actually observed support the idea that the action of ammonia gas on thiophosphoryl fluoride may be represented by the equation—



and if the analogy between Gladstone and Holmes's compound is assumed to hold good, the product, excluding the ammonium fluoride, should be acted upon by water with the formation of thiophosphodiamic acid and hydrofluoric acid, thus:—



In order to obtain further evidence on this point, we passed about half a litre of thiophosphoryl fluoride into a small flask into which a stream of dry ammonia gas was also being led. The solid compound settled on the bottom and sides of the flask as a white, compact crust, which speedily deliquesced on exposure to the air. When freshly prepared it has no smell of ammonia. It dissolves readily in water, giving a slightly alkaline solution, in which no trace of phosphoric acid or hydrosulphuric acid can be detected in the cold. With metallic salts it gives reactions which in some cases correspond with and in others differ from those obtained by Gladstone and Holmes with the solution of the compound obtained by the action of ammonia on thiophosphoryl chloride. Both solutions give precipitates with salts of mercury, copper, silver, lead, and tin, and no precipitate with those of barium and iron. On the other hand, the thiophosphoryl fluoride compound gives no precipitates with salts of zinc, cadmium, nickel, and cobalt, in which respect it differs from the thiophosphoryl chloride compound. Gladstone and Holmes (*loc. cit.*) found that the precipitates obtained from the thiophosphoryl chloride compound consisted of salts of *thiophosphodiamic acid*,  $\text{H}(\text{NH}_2)_2\text{PSO}$ .

On adding copper sulphate solution to a solution of the thiophosphoryl fluoride compound the liquid remains perfectly clear for a short time. A yellowish-white precipitate gradually forms which rapidly darkens in colour and is ultimately transformed into copper sulphide. On filtering, the clear liquid slowly deposits a crystalline salt of a pale greenish-blue colour: it is insoluble in water, both hot and cold, but readily dissolves in dilute hydrochloric acid solution. The salt is only very gradually formed, and many weeks are required to obtain an amount sufficient for analysis. On examination it was found to be a double salt of copper phosphate and copper silicofluoride, of the formula  $\text{Cu}_3\text{P}_2\text{O}_8, \text{CuSiF}_6$ .

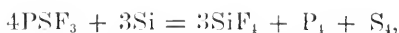
0.3226 gram salt gave 0.1756 CuO and 0.1217  $\text{Mg}_2\text{P}_2\text{O}_7$ .

	Found.	Calculated.
Copper .....	43.15	43.41
Phosphorus .....	10.61	10.53

The formation of this compound is easily accounted for. All the sulphur is removed as copper sulphide and the amidated phosphoric acid is gradually decomposed, with the deposition of the light green double salt, by the hydrofluosilicic acid gradually formed by the action of the hydrofluoric acid on the glass vessel. It is worthy of note that in the double salt the phosphorus bears the same ratio to fluorine that it does in the thiophosphoryl fluoride from which it was derived.

*Action of Thiophosphoryl Fluoride on heated Glass.*—When a quan-

tity of thiophosphoryl fluoride is heated in a glass tube, the gas, after a given temperature has been reached, deposits a yellow film on the glass, the volume begins steadily to decrease, and after a time becomes constant. The residual gas, after the action is complete, consists entirely of silicon tetrafluoride. The decomposition follows the equation—



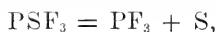
four volumes of the thiophosphoryl fluoride giving three of silicon tetrafluoride. A small measured quantity of thiophosphoryl fluoride was heated in a *cloche courbe* over mercury. After heating for about an hour the tube was allowed to cool and the volume of the residual gas noted. The results of two experiments carried out in this way were as follows:—

- I. 7.90 c.c.  $\text{PSF}_3$  gave 5.95 c.c.  $\text{SiF}_4$ .  
 II. 11.39     ,,     ,,     8.81     ,,

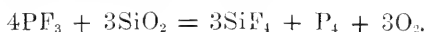
Calculated from the equation—

I .....	5.93 c.c.
II.....	8.65   ,,

The sulphur is rapidly deposited from the heated gas which, indeed, appears first to decompose in accordance with the equation—



the phosphorus trifluoride then decomposing in the manner indicated by Moissan (*Ann. Chim. Phys.* [6], 6, 464),



A portion of the phosphorus combines with sulphur, whilst another part is oxidised and unites with the bases of the glass, forming pyrophosphates or metaphosphates. The deposit on the extreme upper part of the tube is yellow, and inflames on being heated in the air; it dissolves in water with separation of a little silica, and the solution smells of sulphuretted hydrogen, and gives the reactions for phosphoric acid.

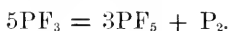
*Action of the Electric Spark and heated Platinum on Thiophosphoryl Fluoride.*—If electric sparks are passed between platinum terminals in an atmosphere of thiophosphoryl fluoride, the gas is at once decomposed. A light yellow substance settles on the platinum wires and on the sides of the containing vessel, and the volume of the gas slowly diminishes. On heating a spiral of platinum to a low red heat in a confined volume of the gas, a cloud at once appears and a yellow film quickly settles on the cold sides of the tube. If the gas stands over

mercury a black sublimate of mercuric sulphide is also formed. The platinum is rapidly attacked, and in two or three minutes falls to pieces, being converted into a black, brittle mass from the action of the phosphorus and sulphur. The yellow deposit consists of sulphur and phosphorus, the former substance occurring in by far the larger quantity. If moisture has been carefully excluded, the residual gas contains no trace of silicon; although its volume is slightly less than that of the thiophosphoryl fluoride taken, it contains only phosphorus and fluorine.

It would thus appear that by the action of heat thiophosphoryl fluoride is quickly decomposed with separation of sulphur and formation of phosphorus trifluoride,



and that the phosphorus trifluoride, as already shown by Moissan (*loc. cit.*), is, by the further action of heat, gradually converted into phosphorus pentafluoride with separation of phosphorus—



*Spectrum of Thiophosphoryl Fluoride.*—Professor J. Norman Lockyer was good enough to instruct Mr. Fowler to make some observations on this point for us. A large end-on tube was carefully filled with dry nitrogen and placed in connection with an apparatus containing a mixture of lead fluoride and freshly made phosphorus sulphide. The tube and apparatus were then exhausted by the Sprengel pump, and the whole filled with the thiophosphoryl fluoride which was then removed by the action of the pump: the filling was repeated once or twice, and the gas finally slowly pumped out until a spark at the lowest possible temperature would pass. As soon as the spark begins to pass the spectrum is found to consist of lines characteristic of the fluorine spectrum as seen in silicon fluoride and boron fluoride. After a time, as the pressure is reduced, lines of phosphorus appear and entirely displace the fluorine spectrum. On further reducing the pressure, the phosphorus lines give place to a spectrum consisting entirely of sulphur flutings. Thiophosphoryl fluoride is therefore dissociated at the lowest temperature of the spark.

*Liquefaction of Thiophosphoryl Fluoride.*—In the Cailletet apparatus, the gas is readily reduced to a colourless, transparent liquid. By means of a specially constructed apparatus, in which we compared the reduction of the volume of hydrogen and of the gas by submitting both to the same pressure, we find the following relation between the temperature and pressure under which the liquefaction of thiophosphoryl fluoride takes place.



Temperatures.	Pressure in atmospheres.
3.8°	7.6
10.0	9.4
13.8	10.3
20.3	13.0

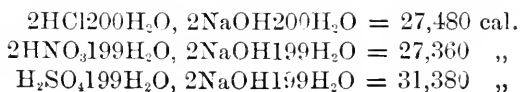
*Addendum.*—In the discussion which followed the reading of this paper, Professor Ramsay suggested that thiophosphoryl fluoride would probably be resolved by shock if treated in the same manner as carbon disulphide vapour, *i.e.*, if a small quantity of mercuric fulminate was exploded in the gas. On making the experiment according to the method already described by one of us (Thorpe, "Decomposition of Carbon Disulphide by Shock," *Trans.*, 1889, 220), a black deposit of mercuric sulphide was instantly produced by the explosion, and in quantity sufficient to show that the whole of the sulphur was thrown out of combination. It is, however, impossible to say definitely whether this result is the direct effect of the explosion or whether it is due to the action of the heated mercury vapour on the gas; in other words, we have no means of knowing whether the action is purely chemical or is merely mechanical.

#### XXXV.—*Note on the Heat of Neutralisation of Sulphuric Acid.*

By SPENCER UMFREVILLE PICKERING, M.A.

It is well known that the heat of neutralisation of acids and alkalis is, in the majority of cases, a constant quantity, though there are several exceptions to the rule. Those cases where the values are abnormally low present no great difficulties, for they are confined chiefly to weak acids where the salts are partially dissociated, and neutralisation is, therefore, not complete; of the existence of abnormally high values (sulphuric, hydrofluoric, hypophosphorous, and selenic acids) I have suggested a possible, though conjectural explanation, based on peculiarities in the amount of the residual affinity possessed by the acids (*Trans.*, 1887, 598). The object of the present note is to give a simpler and more satisfactory explanation of such exceptions. The heat of neutralisation of these acids is *not* abnormally high.

The values given by Thomson for the three commoner acids are:—



the first two being instances of the normal value, the last being 4000 cal. too large.

Any constancy observed in the heat of neutralisation is dependent, as I have shown, on the saturation of the residual affinity of the molecules concerned by the water present, and, hence, this water must be present in large excess, and should, theoretically, be infinite in quantity. Though, with hydrochloric acid, the 200  $\text{H}_2\text{O}$  present is sufficient to practically complete the thermal effects of dilution, this is by no means the case with sulphuric acid. We can calculate what the heat of neutralisation would be in infinity of water by the aid of Thomsen's results on the dilution of the solutions concerned. Thomsen gives the values of the heat evolved (per gram-molecular proportion of the substance present) on diluting solutions of various strengths down to the strength of the weakest solution which he obtained in any given series (*Thermochem. Untersuch.*, III); by plotting these values against the percentage composition we get a curve which may easily be produced to 0 per cent., that is, to infinite dilution. If this point be  $x$  cal. below the zero point which he took, all his values must be increased by  $x$  cal., and they will then express the molecular heat of dissolution of the solution taken in infinity of water. The values which are marked by an asterisk in the accompanying table give the values of  $x$  in the various cases, the others are the values required in the following calculations.

Solution.	Percentage composition.	Molec. heat of dissolution in infinity of water.
* $\text{H}_2\text{SO}_4$ 1799 $\text{H}_2\text{O}$ ....	0.339	+173 cal. (Thomsen).
" .....	"	+2128 " (Pickering).
$\text{H}_2\text{SO}_4$ 199 $\text{H}_2\text{O}$ .....	2.663	+965 " = A (Thomsen).
" .....	"	+3245 " = A' (Pickering).
*2HCl 600 $\text{H}_2\text{O}$ .....	0.670	+164 " (Thomsen).
2HCl 200 $\text{H}_2\text{O}$ .....	2.000	+242 " = E (Thomsen).
*2 $\text{HNO}_3$ 640 $\text{H}_2\text{O}$ ....	1.090	+148 " "
2 $\text{HNO}_3$ 199 $\text{H}_2\text{O}$ ....	3.400	+288 " = F "
*2NaOH 400 $\text{H}_2\text{O}$ ....	1.100	-142 " "
2NaOH 199 $\text{H}_2\text{O}$ ....	2.190	-264 " = B "
2NaOH 200 $\text{H}_2\text{O}$ ....	2.170	-262 " = C "
* $\text{Na}_2\text{SO}_4$ 800 $\text{H}_2\text{O}$ ....	0.980	-102 " "
$\text{Na}_2\text{SO}_4$ 400 $\text{H}_2\text{O}$ ....	1.900	-202 " = D "
*2NaCl 400 $\text{H}_2\text{O}$ .....	1.600	-86 " "
2NaCl 402 $\text{H}_2\text{O}$ .....	1.590	-84 " = G "
*2 $\text{NaNO}_3$ 400 $\text{H}_2\text{O}$ ....	2.300	-368 " "
2 $\text{NaNO}_3$ 402 $\text{H}_2\text{O}$ ....	2.300	-368 " = H "

Now, if we imagine two cycles of operations, in one of which we

mix the strong (with 200 H<sub>2</sub>O) acid and alkali solutions, and then dilute the resulting solution to infinity, and in the other of which we dilute the acid and alkali to infinity first, and then mix them together, the sum of the thermal results in the two cycles will be the same, for the initial and final states are identical: thus:—

$$N + G = E + C + N_{\infty},$$

N being the heat of neutralisation with strong solutions,  $N_{\infty}$  that with infinitely weak ones. Substituting the values given in the table for the other letters, we get  $N_{\infty}$  for 2HCl to be 27,416 cal., practically the same as with strong solutions. For sulphuric acid, Thomsen's values for the equation  $N + D = A + B + N_{\infty}$  give  $N_{\infty} = 30,477$  cal., thus reducing the excess by 900 cal., but leaving it still too great to be called normal.

I have, however, made a much more extensive series of determinations of the heat of dilution of sulphuric acid than that made by Thomsen; the results will be brought before the Society before long, and I need only give here the particular value required for our present purposes,  $A'$  in the foregoing table. Using this value instead of A we get 28,197 cal. for the heat of neutralisation of sulphuric acid, a quantity within 800 cal. of that of hydrochloric acid.

The difference of 2300 cal. between Thomsen's and my own value for the dilution of H<sub>2</sub>SO<sub>4</sub>.199H<sub>2</sub>O may appear very large, but it is not due to simple experimental error. There certainly appears to be some error in Thomsen's determination with the weakest solution which he used, his value being 193 cal. lower than mine (a quantity representing, however, only  $\frac{1}{160}$ th of a degree in the experiment itself), but this would not account for the discrepancy; the fact is that there is a sudden change in the direction of the curve at about 0.3 per cent., and as Thomsen's last determination was made with a 0.67 per cent. solution, his results cannot take this change into account; had I deduced the correction from my own experiments, taking only the same points as Thomsen took, I should have got 29,825 cal. for  $N_{\infty}$ , a value still 2200 cal. above that of hydrochloric acid.

From the equation  $N + H = F + B + N_{\infty}$  we get 26,268 cal. for the heat of neutralisation of nitric acid in infinity of water. Compared with this, my value for sulphuric acid is 1290 cal. too high, but the results are more doubtful in this case, as the correction for the dilution of sodium nitrate is a large one, and the weakest solution used by Thomsen contained as much as 4.5 per cent. of the salt.

A difference of even this magnitude must be considered as within the limits of experimental error. The values for  $N_{\infty}$  in the three cases depend not only on Thomsen's determinations of N (which no doubt are accurate), and on my curve for sulphuric acid, but also on extrapolation from six of Thomsen's curves where the points available

are far too few to give more than approximate values. There can be little doubt but that the heat of neutralisation of sulphuric acid, and probably also that of selenic, hypophosphorous and hydrofluoric acids,\* is normal, under perfect conditions, and it must be remembered that these perfect conditions include, not only infinite dilution, but also some appropriate temperature, probably the absolute zero, for the heat of neutralisation is affected to different extents in different cases by altering the temperature, and absolute identity of results at  $18^{\circ}$  would imply non-identity at other temperatures. Under these perfect and unattainable conditions, the value would be constant only because we should be measuring the *same* quantity in every case, namely, the difference between (a) the heat of combination of H with (OH) and the union of the water molecules with each other, and (b) the heat of combination of M with (OH) and the union of the hydroxide formed with excess of water, which latter quantity is the same whatever metal M may be, for it represents in each case the perfect satisfaction of the affinity of the same radicle—hydroxyl (see Trans., 1888, 878).

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XXXVI.—*The Boiling Points of Sodium and Potassium.*

By E. P. PERMAN, B.Sc., Clothworkers Exhibitioner at University College, London.

As no attempts seem to have been made hitherto to determine with any degree of accuracy the boiling points of sodium and potassium, I undertook, at Prof. Ramsay's suggestion, to ascertain these constants.

*Method employed.*—About 10 grams of sodium were heated in a combustion-tube, sealed at one end, and placed vertically over a Bunsen flame: the metal melted but gave off very little vapour. On raising the temperature by using a blowpipe, the sodium began to boil, but soon attacked and perforated the tube. A second trial with a thicker tube gave the same result. An iron tube was then substituted for the glass one with somewhat better success; the sodium was made to boil, and a small bulb of combustion-glass, with a long, capillary stem, was hung in the vapour, and the end sealed by means of a hand-blowpipe, when the sodium vapour was supposed to have reached the neck of the bulb. The results were unsatisfactory, and it was found much better to use a hollow iron ball surrounded by a screen of fireclay, and to heat it with one of Fletcher's blowpipes such as are sold with his injector furnaces. The sodium soon boiled

\* There are no data for calculating the corrections in these cases.

and the vapour issued from the hole in the top of the iron ball, and burned. The size of the flame indicated the rate at which the metal was boiling. Several bulbs were lowered into the vapour, some of combustion-glass and some of ordinary glass; the latter were found to answer quite as well as the former. Each bulb was held so that the sodium flame played round its neck for about half a minute; it was then lowered till completely surrounded by the vapour, held thus for a few seconds, the end sealed, and withdrawn. In the case of potassium, the injector blowpipe was unnecessary, an ordinary blowpipe easily producing the required temperature. The method of procedure was the same.

The bulbs were afterwards boiled in water to remove potash or soda, carefully dried, and weighed. Some were deeply etched and leaked; but a sufficient number survived to give reliable results. The capillary stems were broken under boiled water, the pieces broken off being weighed separately, and the weight of each being added to that of its bulb; the bulbs were immersed in the water and the temperature taken; they were then again dried and weighed. The volume of expelled air is given by that of the water entering the bulb. They were lastly boiled under water till full, cooled to about  $20^{\circ}$  (slightly above the temperature of the laboratory in order to avoid loss by expansion during the weighing), dried, and weighed. This gave the capacity of each bulb.

#### *Method of Calculation.*

Let  $w_1$  be the weight of water in the bulb after breaking the stem,

$w_2$  weight of water required to fill the bulb,

$t^{\circ}$  the required temperature,

$t_1^{\circ}$  temperature of water on removing bulb after breaking the stem,

$\alpha$  coefficient of comparison of air = 0.003667,

$\delta$  " " of glass = 0.00003,

$d_1$  density of water at temperature  $t_1^{\circ}$ ,

$d_2$  " " "  $t_2^{\circ}$ ,

$p_1$  atmospheric pressure on sealing the bulb,

$p_2$  atmospheric pressure on breaking the stem, minus the vapour-pressure of water at  $t_1^{\circ}$ .

Then the volume of air in the bulb at temp.  $t_1^{\circ}$  and pressure  $p_1$  is

$\frac{w_2}{d_2} - \frac{w_1}{d_1}$ , and this at the temp.  $t^{\circ}$  and pressure  $p_2$  expands to

$\frac{p_2}{p_1} \left( \frac{w_2}{d_2} - \frac{w_1}{d_1} \right) \frac{1 + \alpha t}{1 + \alpha t_1}$ , but it then fills the bulb, which has the

volume  $\frac{w_2}{d_2} \frac{1 + \delta t}{1 + \delta t_2}$  at the temp.  $t^{\circ}$ ,

$$i.e., \frac{p_2(w_2 - w)}{p_1(d_2 - d_1)} \frac{1 + \alpha t}{1 + \alpha t_1} = \frac{w_2}{d_2} \left( \frac{1 + \epsilon t}{1 + \epsilon t_2} \right).$$

Now  $d_1$  and  $d_2$  were always practically identical, for  $t_1$  and  $t_2$  never differed by more than  $2^\circ$ . The expression then becomes—

$$\frac{p_2 w_2 - w_1}{p_1 1 + \alpha t_1} (1 + \alpha t) = \frac{w_2}{1 + \epsilon t_2} (1 + \epsilon t).$$

$$\text{Put } \frac{p_2 w_2 - w_1}{p_1 1 + \alpha t_1} = A \text{ and } \frac{w_2}{1 + \epsilon t_2} = B, \text{ and we find } t = \frac{B - A}{A\alpha - B\epsilon}.$$

From this expression all the results were calculated.

The *actual data* obtained are—

- a. Weight of bulb + air.
- b. „ „ + air + water.
- c. „ „ + water.
- d. „ capillary stem broken off.

Also  $t_1$ ,  $t_2$ ,  $p_1$ , and  $p_2$ .

The bulb contains the same weight of air in *a* and *b*; therefore, to find  $w_1$ , subtract *a* from *b* and add *d*. To find  $w_2$ , subtract *a* from *c*, add *d*, and also add the weight of the enclosed air, roughly estimated from the volume of the bulb.

The numerical data and the calculated results are here tabulated:—

	Sodium.			Potassium.		
	1.	2.	3.	1.	2.	3.
<i>a</i> ....	1.9015 grams	1.1345	0.8003	1.2740	1.6441	1.6411
<i>b</i> ....	2.4715 „	1.6890	1.2245	2.0044	2.2398	2.4516
<i>c</i> ....	2.7238 „	1.9308	1.4085	2.3705	2.5528	2.8493
<i>d</i> ....	0.0170 „	0.0037	0.0038	0.0263	0.0385	0.0125
$t_1$ ....	21°	20°	20°	22.5°	21.5°	21.5°
$t_2$ ....	20°	20°	20°	20°	20°	20°
$p_1$ ....	769.6 mm.	769.6	769.6	759.8	759.8	759.8
$p_2$ ....	756.1 „	756.1	756.1	739.6	740.8	740.8
$w_1$ ....	0.5870 gram	0.5582	0.4280	0.7567	0.6342	0.8230
$w_2$ ....	0.8396 „	0.8003	0.6122	1.1236	0.9480	1.2217
<i>t</i> ....	746°	737°	742.5°	674°	656°	670°

Mean result for sodium ..... 742°.  
 „ for potassium ..... 667°.

*Possible Errors.*—Superheating of the vapour may cause an error perhaps of  $10^\circ$ , or more if the metal is nearly volatilised.

The weighings were accurate to 0.2 milligram, the temperatures

were read to  $0.1^\circ$  and the pressures to 0.1 mm., so that the errors have no appreciable effect on the value of  $t$ .

The non-exposure of the capillary stem to the vapour causes a small error, which is in the opposite sense to the error caused by super-heating.

There is a possible error in the number taken for the coefficient of expansion of the glass used, but an error of 20 per cent. (0.000030 instead of 0.000025) would only cause an error of  $2^\circ$  or  $3^\circ$  in the boiling point found. The coefficient was carefully determined for the glass of which the bulbs were made. A bulb of about 4 c.c. capacity was weighed, then filled with boiled mercury and boiled out several times, cooled, placed in water at a slightly higher temperature,  $t_1$ , weighed, hung over boiling water, and weighed again. The coefficient of expansion,  $\hat{e}$ , was calculated from the equation

$$\frac{1 + \hat{e}t_1}{1 + \hat{e}t_2} = \frac{w_1}{w_2} \frac{1 + at_1}{1 + at_2},$$

where

$w_1$  = weight of mercury filling bulb at  $t_1^\circ$ .

$w_2$  = " " " "  $t_2^\circ$ .

$a$  = coefficient of absolute expansion of mercury between  $0^\circ$  and  $t_2^\circ$ .

The bulb was also hung over boiling mercury and weighed again.

The data and results are:—

	Temperature.	Weight.	$\delta$ .
Bulb + air. ....	—	3.1795 gram	—
" + mercury .....	$19.7^\circ$	53.2503 "	—
" + " .....	$99.4$	52.6410 "	0.000027
" + " .....	$358.2$	50.6754 "	—
" + " .....	"	50.7120 "	—
" + " .....	"	50.6820 "	0.000028

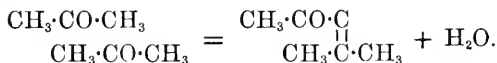
The boiling points were found to be not far from  $700^\circ$ , and  $\delta$  was therefore taken as 0.00003, assuming its value to increase regularly with rise of temperature. The difference in the weights at  $358^\circ$  was due to traces of air which remained in the bulb; the highest number was taken as correct.

*Remarks.*—The results given by sodium agree much better than those obtained for potassium. The reason probably is that a much smaller quantity of potassium was used than of sodium; further, it boiled away, and more lumps had to be thrown into the ball, so that in this case the method is very much the same as if one threw a lump of ice into a hot vessel and immediately tried to find the boiling point of water.

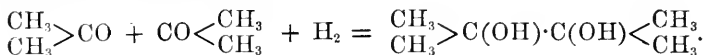
XXXVII.—*αω-Diacetylpentane and αω-Dibenzoylpentane.*

By F. STANLEY KIPPING, Ph.D., D.Sc., and W. H. PERKIN, Jun., Ph.D.

UNDER the influence of dehydrating agents, acetone readily undergoes condensation with formation of mesityl oxide, phorone, and other substances. The reaction in the case of mesityl oxide is represented by the equation—



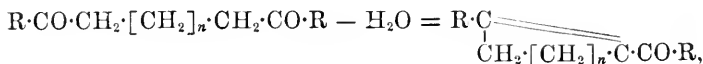
Furthermore, when acetone is treated with certain reducing agents it yields pinacone, thus:—



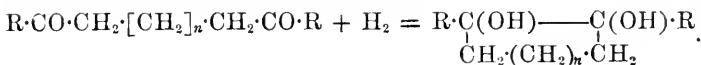
In each of these reactions, 2 mols. of acetone take part, the resulting compounds being formed by the direct union of two carbon-atoms, one from each molecule.

In studying these curious reactions, it seemed possible that, starting with diketones of the formula  $\text{R}\cdot\text{CO}\cdot\text{CH}_2\cdot[\text{CH}_2]_n\cdot\text{CH}_2\cdot\text{CO}\cdot\text{R}$ , and subjecting them to similar treatment, the condensation might be confined to one molecule.

Thus, under the influence of dehydrating agents, the change would be—



whereas a reduction analogous to the formation of pinacone from acetone would take the following course:—



With the object of testing this hypothesis, we have prepared *αω*-diacetylpentane,  $\text{CH}_3\cdot\text{CO}\cdot[\text{CH}_2]_5\cdot\text{CO}\cdot\text{CH}_3$ , *αω*-dibenzoylpentane,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot[\text{CH}_2]_5\cdot\text{CO}\cdot\text{C}_6\text{H}_5$ , and *αω*-diacetylbutane,



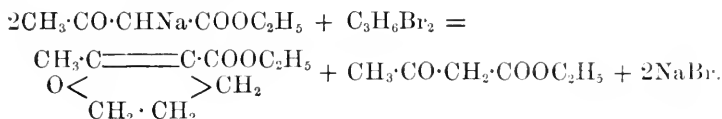
and have nearly completed our experiments on the behaviour of these compounds towards dehydrating and reducing agents. In the present paper, we describe the preparation and properties of *αω*-diacetylpentane and the corresponding dibenzoyl-compound, and give also a



short account of several less important substances which have been obtained in the course of this investigation.

*Preparation of Ethyl Methyldehydrohexoncarboxylate and Acetobutyl Bromide.*

In previous researches in which ethyl methyldehydrohexoncarboxylate has been employed, this substance was always prepared by treating 2 mols. of ethyl acetoacetate with 2 mols. of sodium ethylate and 1 mol. of trimethylene bromide, thus:—



The objection to this method is, that one-half of the ethyl acetoacetate is regenerated, and this on subsequent fractionating can be separated only very partially from the ethyl methyldehydrohexoncarboxylate, and is thus practically wasted.

As it was necessary for us to employ large quantities of this substance, we have made a number of experiments with a view to improve the method of preparation. As the result of these we find the following process to give the best results:—

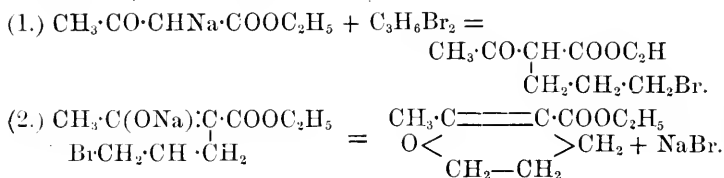
130 grams of ethyl acetoacetate are added in small quantities at a time to a cold solution of 23 grams of sodium in 250 grams of absolute alcohol, care being taken that the temperature of the mixture does not rise above  $40^\circ$ ; 202—205 grams of trimethylene bromide are now added, and the whole heated to boiling in a water-bath, in a flask connected with a reflux apparatus. As soon as the solution begins to boil, the separation of sodium bromide commences and a vigorous reaction sets in, the heat evolved being sufficient to keep the whole boiling for a considerable time.

After heating for about  $1\frac{1}{2}$  hours, the product is well cooled and gradually mixed with a further quantity of 23 grams of sodium in 250 grams of absolute alcohol: the same precautions as to temperature being observed as in the first instance. The contents of the flask are again heated in the water-bath, when a further separation of sodium bromide occurs. After boiling for about an hour the alcohol is distilled off, the residue mixed with water, the product extracted twice with a large quantity of ether, and the ethereal solution washed, dried over calcium chloride, and evaporated. The oily product, which should weigh from 155 to 160 grams, is distilled at the ordinary pressure, and the following fractions collected:—

80--200°	= about 15 grams.
200--240	= 128--133 grams.
Residue	= about 10 grams.

The thermometer rises rapidly to 200°, only small quantities of alcohol, ether, and a little unchanged trimethylene bromide passing over below this temperature, a proof that practically the whole of the ethyl acetoacetate had been converted into ethyl methyldehydrohexone-carboxylate.

The fraction 200--240° is an almost colourless oil, which consists, in spite of the wide range of temperature, of nearly pure ethyl methyldehydrohexonecarboxylate, the yield of which is generally 83 to 86 per cent. of the theoretical, and in some cases, with very careful working, as much as 90 per cent. has been obtained. Its formation by this new method is represented by the equations—



The high boiling residue left in the retort is probably the product of the action of 2 mols. of ethyl acetoacetate on 1 mol. of trimethylene bromide. It is at present under investigation.

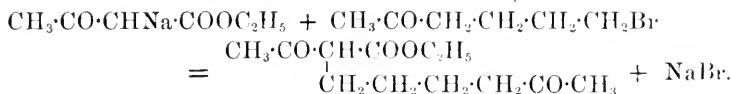
*Acetobutyl Bromide*,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$ .

In preparing acetobutyl bromide, the fractionated ethylic methyldehydrohexonecarboxylate is dissolved in about three times its volume of a saturated solution of hydrogen bromide (sp. gr. about 1.7), and the mixture allowed to stand for 24 hours. The whole is then poured into a large volume of cold water and the precipitated oil separated. The solution still contains a considerable quantity of the bromide, which can be completely extracted with ether if the solution is first neutralised with soda. The separated oil and the ethereal solution are mixed together, washed with dilute sodium carbonate solution, dried over calcium chloride, and the ether distilled off.

The acetobutyl bromide is thus obtained as a brownish oil, the yield of the crude product being about 86 per cent. of the theoretical. The crude bromide is now fractioned under diminished pressure, when the greater portion distils at a constant temperature (under 150 mm. at 155--160°; under 90 mm. at 135--137°), leaving as a residue a dark-brown oil, amounting to about 16 to 20 per cent. of the whole.

*Ethyl  $\alpha\omega$ -Diacetylcaproate.*

When acetobutyl bromide is warmed with an alcoholic solution of ethyl sodacetoacetate, sodium bromide separates, and ethyl  $\alpha\omega$ -diacetylcaproate is formed, thus:—



In preparing this substance, 80 grams of ethylic acetoacetate were dissolved in a solution of 14 grams of sodium in 150 grams of absolute alcohol, 110 grams of acetobutyl bromide added, and the whole heated on a water-bath in a flask connected with a reflux condenser. As soon as the mixture came to the boiling point, sodium bromide began to separate, and in a very short time the reaction was at an end. The alcohol was distilled off, the residue mixed with water, the product extracted twice with ether, the ethereal solution washed with water, dried over calcium chloride, and the ether evaporated.

The thick, oily residue, which weighed 144 grams, was readily purified by fractionation under reduced pressure.

The pure substance boiling at  $238\text{--}242^\circ$  (200 mm. pressure) gave the following result on analysis:—

0.1435 gram substance gave 0.3333 gram  $\text{CO}_2$  and 0.1174 gram  $\text{H}_2\text{O}$ .

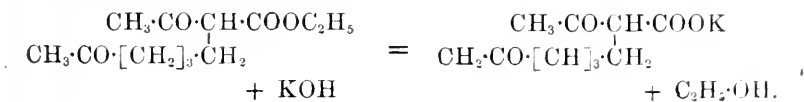
	Calculated for $\text{C}_{12}\text{H}_{20}\text{O}_4$ .	Found.
C .....	63.16 per cent.	63.34 per cent.
H .....	8.77     "	9.09     "
O .....	28.07     "	27.57     "

Ethyl  $\alpha\omega$ -diacetylcaproate is a thick, colourless oil, having a faint odour. It is almost insoluble in water, but readily miscible with ether and alcohol.

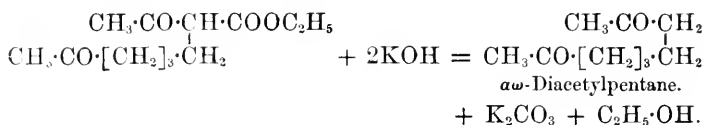
*Hydrolysis of Ethyl  $\alpha\omega$ -Diacetylcaproate.*

The action of caustic potash on ethyl  $\alpha\omega$ -diacetylcaproate may take place in one of the following three ways, according to the conditions of the experiment:—

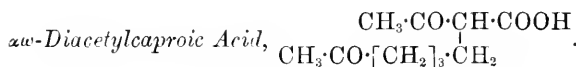
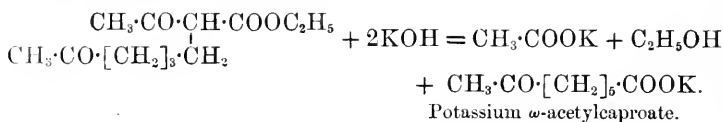
1st. When the ethereal salt is mixed with an excess of a solution of strong potash in methyl alcohol and allowed to stand in the cold,  $\alpha\omega$ -diacetylcaproic acid is formed, thus:—



2ndly. When the ethereal salt is hydrolysed by boiling with dilute alcoholic potash,  $\alpha\omega$ -diacetylpentane is formed, thus:—



3rdly. When the hydrolysis takes place in the presence of a large excess of boiling alcoholic potash, besides  $\alpha\omega$ -diacetylpentane,  $\omega$ -acetylcaproic acid is formed, thus:—



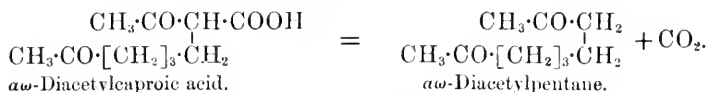
This acid is prepared by dissolving the crude ethereal salt in an excess of a cold saturated solution of pure potash in methyl alcohol, and allowing the mixture to stand for 24 hours. The resulting slightly brownish solution is placed over sulphuric acid in a vacuum until nearly all the alcohol has evaporated, the residue dissolved in water and repeatedly extracted with ether to remove traces of diacetylpentane which are invariably formed during the reaction. The alkaline solution is carefully acidified with dilute sulphuric acid, the clear liquid extracted several times with pure ether, the ethereal extract dried over calcium chloride and evaporated at a low temperature on a water-bath. The resulting slightly yellowish oil, after the removal of the last traces of ether, consists of nearly pure  $\alpha\omega$ -diacetylcaproic acid, as the following analysis shows:—

0.1769 gram substance gave 0.3886 gram  $\text{CO}_2$  and 0.1326 gram  $\text{H}_2\text{O}$ .

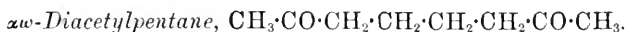
	Calculated for $\text{C}_{10}\text{H}_{16}\text{O}_4$ .	Found.
C .....	60.00 per cent.	59.91 per cent.
H .....	8.00     "	8.33     "
O .....	32.00     "	31.76     "

Diacetylcaproic acid is miscible with water in all proportions, the solution reacting strongly acid; the addition of a drop of ferric chloride to this solution produces a slight brownish-violet coloration. If a small quantity of the acid is gently heated in a test-tube, car-

bonic anhydride is evolved, and the resulting oil, on distillation, solidifies on the cooler portions of the tube to colourless plates consisting of pure  $\alpha\omega$ -diacetylpentane :—



The salts of diacetylcaproic acid are mostly readily soluble in water and difficult to prepare in a pure condition. The *silver* salt is a colourless, seemingly amorphous compound, readily soluble in cold water. In an aqueous solution of the ammonium salt, ferric chloride produces a light brown precipitate, which is quickly decomposed on heating; lead acetate gives no precipitate in dilute solutions, but copper sulphate produces a light green precipitate readily soluble in warm water. Mercuric nitrate gives a white precipitate which quickly dissolves when the solution is warmed.



In the first attempts at preparing this diketone, ethyl  $\alpha\omega$ -diacetylcaproate (1 mol.) was mixed in the cold with a dilute solution of potash (2 mols.) in methyl alcohol, and after standing for two days a further quantity of potash (4 mols.) was added, and the mixture boiled for six hours. After distilling off the alcohol, the residue was dissolved in water, the product extracted with ether, the ethereal solution dried over calcium chloride and evaporated. A slightly yellowish oil was obtained containing, besides diacetylpentane, a second substance which is with difficulty separated by fractional distillation. It could be removed, however, by shaking with sodium hydrogen sulphite solution, collecting the solid double compound with diacetylpentane which is formed, washing this with ether, and decomposing with sodium carbonate. In this way a beautiful crystalline substance was obtained which gave the following numbers on analysis :—

0.1528 gram substance gave 0.3890 gram  $\text{CO}_2$  and 0.1435 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_9\text{H}_{16}\text{O}_2$ .	Found.
C . . . . .	69.23 per cent.	69.4 per cent.
H . . . . .	10.26     „	10.4     „
O . . . . .	20.51     „	20.2     „

As this process was very inconvenient for the preparation of large quantities of this substance, experiments were made with the object of improving the yield, and as a result the following method was found to give the largest quantity of pure diketone.

Rather more than the calculated quantity of potash required for hydrolysis (2 mols.) is dissolved in a little methyl alcohol, with the addition of a few drops of water; about one third of this solution is mixed with the ethyl diacetylcaproate and the mixture heated to boiling on the water-bath, in a flask connected with a reflux apparatus, for about five minutes, during which operation a quantity of potassic carbonate separates. Another third of the alcoholic potash is now added and the heating continued. In about 10 minutes the remainder of the potash is poured in, the alcohol at once distilled off and the residue mixed with water.

The product is extracted two or three times with ether, the extract dried over calcium chloride, and the ether evaporated. In this way an almost colourless residue is obtained which may readily be purified by fractionation under reduced pressure.

The approximate yield of the crude substance is 50–52 grams from 100 grams ethyl diacetylcaproate. This oil on fractioning behaves somewhat curiously. Thus, under a pressure of 300 mm. the thermometer rises rapidly to  $170^{\circ}$ , between which temperature and  $190^{\circ}$  about 5 per cent. distils, as a colourless oil which on cooling shows no signs of solidifying. The distillate between  $190^{\circ}$  and  $219^{\circ}$  solidifies entirely, and forms about 90 per cent. of the whole, and on several occasions it was noticed that although the substance gave good numbers on analysis it still possessed no constant boiling point. In order if possible to settle this point, the pure solid substance was refractioned under 240 mm. pressure without, however, any very definite boiling point being noticed. In fractioning large quantities, the nearest approach to a constant boiling point has been  $212$ – $215^{\circ}$  (300 mm.), and  $175$ – $178^{\circ}$  (130 mm.).

An analysis of the substance fractioned in this way gave the following numbers:—

0.1725 gram substance gave 0.4367 gram  $\text{CO}_2$  and 0.1617 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_9\text{H}_{16}\text{O}_2$ .	Found.
C .....	69.23 per cent.	69.04 per cent.
H .....	10.26     ,,	10.41     ,,
O .....	20.51     ,,	20.55     ,,

$\alpha\omega$ -Diacetylpentane, purified by washing with ether on a porous plate, melts at about  $48$ – $49^{\circ}$ . It is readily soluble in cold ether, alcohol, acetone, chloroform, and warm light petroleum. Small particles thrown on to water move about rapidly with a rotatory motion, and gradually dissolve; but separate again on the addition of potassic carbonate. When shaken for some time with a saturated

solution of hydrogen sodium sulphite, diacetylpentane gradually combines with it to form a solid, semicrystalline substance which was not analysed. This double compound is soluble in cold water, but when heated with water or treated with acids, the diketone separates as an oil which readily solidifies on cooling.

Diacetylpentane dissolves in a concentrated aqueous solution of hydrogen bromide, and on boiling and adding water a heavy oil is precipitated which smells strongly of peppermint; this is at present under investigation. The diketone dissolves very readily and apparently without decomposition in concentrated nitric acid, but on heating nitrous fumes are evolved, and considerable quantities of an acid, apparently oxalic acid, is formed. The solution of diacetylpentane in chloroform absorbs bromine very rapidly, with evolution of streams of hydrogen bromide. After adding the bromine till a permanent coloration was produced, the solution was allowed to evaporate spontaneously; an oily bromide remained which did not solidify even after long standing and was therefore not analysed.  $\alpha\omega$ -Diacetylpentane dissolves in concentrated sulphuric acid with evolution of heat and formation of a colourless oil which has the composition  $C_9H_{14}O$ . This substance, which is also formed when the diketone is boiled with alcoholic potash, is of considerable interest, and will be fully described in a subsequent paper. The behaviour of diacetylpentane towards reducing agents is also being carefully investigated, and we hope soon to be able to communicate the results of these investigations to the Society.

*$\alpha\omega$ -Diacetylpentanedioxime*,  $CH_3 \cdot C(NOH) \cdot [CH_2]_5 \cdot C(NOH) \cdot CH_3$ .

Before proceeding any further with the investigation of the diacetylpentane it was thought necessary to prove its constitution by the preparation of a dioxime. This substance is readily obtained by treating the diketone in dilute alcoholic solution with a slight excess of hydroxylamine hydrochloride and potassic carbonate. After standing for two days at the ordinary temperature, water was added, the clear solution extracted with ether, the extract washed with water, dried over calcium chloride, and the ether evaporated. The resulting colourless viscid oil was placed over sulphuric acid under diminished pressure, to crystallise. The crystalline cake thus obtained was spread on a porous plate to remove traces of oily mother-liquor, and further purified by recrystallisation from a mixture of benzene and light petroleum.

The analysis gave the following results :—

1. 0.1770 gram substance gave 0.1582 gram  $H_2O$  and 0.3764 gram  $CO_2$ .

II. 0.1745 gram substance gave 23.3 c.c. N at 16° and 752 mm.

	Calculated for $C_9H_{18}N_2O_2$ .	Found.	
		I.	II.
C .....	58.06 p. c.	57.99	— p. c.
H .....	9.68 „	9.92	— „
N .....	15.05 „	—	15.34 „
O .....	17.21 „	—	—

Diacetylpentanedioxime separates from a mixture of boiling benzene and light petroleum, on cooling, in the form of a crystalline powder. From water, in which it is moderately soluble, it separates in colourless moss-like crystals, melting at 84–85°. It is readily soluble in cold acetone, glacial acetic acid, methyl alcohol, and in warm benzene and ethyl acetate, but only sparingly soluble in boiling and almost insoluble in cold light petroleum. It dissolves freely in cold dilute soda and in concentrated sulphuric acid, forming colourless solutions. When heated in small quantity in a test-tube, it distils with very slight decomposition in the form of a yellowish oil, which quickly solidifies.

*$\omega$ -Acetylcaproic Acid*,  $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot COOH$ .

This acid is formed, together with  $\alpha\omega$ -diacetylpentane, when ethyl  $\alpha\omega$ -diacetylcaproate is hydrolysed, as described above, with boiling methyl alcoholic potash, and remains as potassium salt when the diketone is extracted with ether.

To isolate the acid, the alkaline solution is acidified, extracted about 10 times with ether, the ethereal solution dried over calcium chloride, and the ether evaporated. A brown sour-smelling oil is obtained, the quantity of which varies according to the strength of the potash employed. The purification of the crude acid is attended with very considerable loss, as the salts are mostly readily soluble in water, and the acid, when very impure, is almost entirely decomposed when distilled under diminished pressure. Attempts to purify the acid by means of the ethyl salt were also unsuccessful, as when hydrogen chloride is passed into an alcoholic solution of the acid the mixture darkens rapidly, and the product seems to consist of some complicated condensation-compounds containing chlorine.

The acid was obtained in a pure state as follows:—The crude oil is dissolved in excess of boiling baryta, a stream of carbonic anhydride passed through the hot solution, and, after filtering, the solution is acidified and extracted 8 to 10 times with ether. The almost colourless oil which remains, when the ether is distilled, is again dissolved in boiling baryta, and the process repeated. The acid is thus



obtained in the form of a colourless oil, which, however, as was shown by analysis, still contains a large quantity of some compound richer in carbon. It is dissolved in concentrated ammonia, the solution evaporated to dryness at the ordinary temperature, and the residual brownish ammonium salt kept for some time on a porous plate to free it from oily impurities. The colourless salt is dissolved in water, the acidified solution extracted with pure ether, the extract dried over calcium chloride, and evaporated. Acetylcaproic acid remains as a colourless oil, which immediately solidifies to a mass of colourless crystalline plates, melting at  $29-30^\circ$ , and readily soluble in water. This acid has also been obtained by one of us, in conjunction with Dr. Colman, by treating ethyl malonate and sodium ethoxide with acetobutyl bromide, hydrolysing the ethereal salt, and distilling the resulting bibasic acid.

The *silver* salt,  $\text{CH}_3\text{CO}\cdot[\text{CH}_2]_5\text{COOAg}$ , prepared by precipitating a neutral aqueous solution of the ammonium salt with silver nitrate, crystallises from boiling water, in which it is very readily soluble, in colourless plates, and, after drying over sulphuric acid, it was analysed with the following results:—

0.2430 gram of the salt gave 0.0985 gram of silver.

	Calculated for $\text{C}_8\text{H}_{13}\text{O}_3\text{Ag}$ .	Found.
Ag . . . . .	40.68 per cent.	40.53 per cent.

*Action of Alcoholic Ammonia on Ethyl  $\alpha\omega$ -Diacetylcaproate.*

The first attempts to prepare large quantities of pure diacetylpentane were not attended with much success, and it was thought expedient to try and purify the crude ethyl diacetylcaproate by converting it into a crystalline ammonia compound, analogous to that obtained in the case of ethyl diacetyladipate.

The ethereal salt (42 grams) was therefore dissolved in 8–10 volumes of absolute alcohol, the solution saturated with anhydrous ammonia at the ordinary temperature, and kept for about two days. The solution was again saturated with ammonia, and after keeping for three days the alcohol was evaporated over sulphuric acid. A considerable quantity (6 grams) of a crystalline compound gradually separates from the solution. The crystals were filtered from the mother-liquor, spread on a plate to free them from adherent oil, and then boiled with a mixture of ethyl acetate and methyl alcohol insufficient to dissolve more than about half the whole. The residue was completely dissolved in a mixture of ethyl acetate and methyl alcohol, and the crystalline compound which separated on cooling, recrystallised from methyl alcohol. A compound,  $\text{C}_{16}\text{H}_{15}\text{O}_2\text{N}$ , is thus

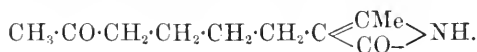
obtained in compact colourless crystals, which, after drying over sulphuric acid, gave the following results on analysis:—

I. 0.1648 gram of substance gave 0.3994 gram  $\text{CO}_2$  and 0.1280 gram  $\text{H}_2\text{O}$ .

II. 0.0917 gram substance gave 5.95 c.c. N at  $12^\circ$  and 750 mm.

	Calculated for $\text{C}_{10}\text{H}_{15}\text{O}_2\text{N}$ .	Found.	
		I.	II.
C .....	66.3 p. c.	66.1	— p. c.
H .....	8.3 „	8.6	— „
N .....	7.7 „	—	7.6 „
O .....	17.7 „	—	—

This substance, as will be shown hereafter, is most probably dehydrodiacetylcapronamide, and has the constitution—



It separates from cold methyl alcohol in large compact crystals, which have been very kindly measured by Professor Haushofer, who gives the following account of his observations:—

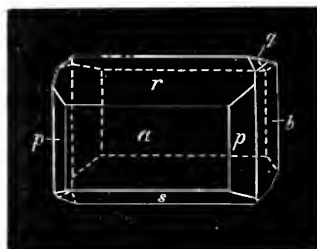
“ Crystalline form *monoclinic*.

$$a : b : c = 0.7487 : 1 : 0.3997.$$

$$\beta = 79^\circ 11'.$$

Plates or small prisms of the combination  $\infty \text{P}\infty(100) = a$ ,  $\infty \text{P}\infty(010) = b$ ,  $-\text{P}\infty(101) = r$ ,  $\text{P}\infty(10\bar{1}) = s$ ,  $\infty \text{P}(110) = p$ , very small, occurring seldom and difficult to measure;  $2\text{P}\infty(021) = q$ .

	Observed.	Calculated.
$a : r = (100)(101) =$	$126^\circ 18'$	—
$a : s = (100)(10\bar{1}) =$	$109 \quad 26$	—
$a : p = (100)(110) =$	$126 \quad 20$	—
$r : s' = (101)(\bar{1}01) =$	$124 \quad 19$	$124^\circ 16'$
$r : s = (101)(10\bar{1}) =$	$55 \quad 49$	$55 \quad 44$
$q : s' = (021)(\bar{1}01) = \text{approx.}$	$133$	$132 \quad 48$
$q : r = (021)(101) =$	$136$	$135 \quad 14 \quad "$

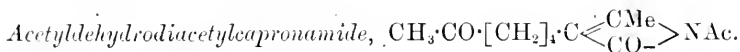


The plane of the optical axes is the plane of symmetry; one axis meets the surface *a*, the other surface *s*, both apparently near the edge *a/s*.

Dehydrodiacetylcaponamide melts at 233–235° with previous softening and slight decomposition, and when heated in small quantities at a higher temperature, it is decomposed with evolution of ammonia, or some volatile base. It is readily soluble in cold glacial acetic acid and in mineral acids, and moderately soluble in hot methyl alcohol and ethyl acetate, but only sparingly in cold benzene, and almost insoluble in boiling acetone. When boiled with water it gradually dissolves, and is partially converted into diacetylcaponamide, which is much more readily soluble; on cooling, a considerable quantity of the dehydro-compound separates immediately in beautiful, short, thick, transparent plates, and the filtrate contains the amide, which separates slowly in flat, transparent, efflorescent plates, when the solution is allowed to evaporate at the ordinary temperature. It is slowly decomposed when boiled with soda, considerable quantities of ammonia being evolved, and the characteristic peppermint smell of the compound  $C_9H_{14}O$  being distinctly perceptible.

The constitution of this compound seems to be proved by the following experiments:—

- (1.) It yields an acetyl-derivative and a nitroso-compound.
- (2.) It is readily hydrolysed by cold alcoholic potash, being converted into  $\alpha\omega$ -diacetylcaproic acid.
- (3.) When boiled with water, it takes up 1 mol.  $H_2O$ , yielding diacetylcaponamide.



When dehydrodiacetylcaponamide is boiled with excess of acetic anhydride for about four hours, it is converted into an acetyl-derivative. To isolate the product, the acetic anhydride is partially removed by distillation, the residue mixed with water, and after keeping for some time the whole extracted two or three times with ether. The ethereal solution is washed with water and sodium carbonate solution until free from acetic acid, dried over calcium chloride, and the ether evaporated.

Acetyldehydrodiacetylcaponamide remains as an almost colourless oil, and as it could not be obtained in a crystalline condition, the crude product was kept over sulphuric acid for about two days and then analysed, with the following results:—

0.1535 gram of substance gave 0.3585 gram  $CO_2$  and 0.1070 gram  $H_2O$ .

	Calculated for $C_{12}H_{17}O_3N$ .	Found.
C .....	64.57 per cent.	63.70 per cent.
H .....	7.62 „	7.74 „
N .....	6.28 „	—
O .....	21.53 „	—

A nitroso-compound was prepared, in small quantity, by treating a cold dilute hydrochloric acid solution of dehydrodiacetylcapronamide with the calculated quantity of sodium nitrite, and extracting the product with ether. A colourless oil was obtained; it dissolved in soda with a transient yellow coloration, but owing to the small quantity at our disposal it was not analysed.

Dehydrodiacetylcapronamide is decomposed by a cold concentrated solution of alcoholic potash, yielding ammonia and  $\alpha\omega$ -diacetylcaproic acid. A small quantity of the dehydro-compound was dissolved in cold methyl alcoholic potash, the solution kept for two days, and the alcohol evaporated at the ordinary temperature. The residue was dissolved in water, the solution extracted with ether to remove any diacetyl-pentane which might have been formed, then acidified with dilute sulphuric acid, and the acid extracted with pure ether. A colourless oil remained when the dried ethereal solution was evaporated, and the crude product, after keeping for 24 hours over sulphuric acid, was analysed with the following results:—

0.1703 gram of substance gave 0.3748 gram  $CO_2$  and 0.1288 gram  $H_2O$ .

	Calculated for $C_{10}H_{16}O_4$ .	Found.
C .....	60.0 per cent.	60.0 per cent.
H .....	8.0 „	8.4 „
O .....	32.0 „	31.6 „

That this acid is in reality diacetylcaproic acid is further proved by the following experiments:—When heated at about  $100^\circ$ , rapid evolution of carbonic anhydride occurs, and on heating more strongly the whole distils in the form of a colourless oil, and quickly solidifies. The solid distillate was found to be identical with diacetyl-pentane, and, like the last-named compound, on boiling with potash it gives out a strong smell of peppermint, due to the formation of the compound  $C_9H_{14}O$ . When the dehydro-compound is boiled with water, it is converted into diacetylcapronamide.

$\alpha\omega$ -Diacetylcapronamide,  $CH_3 \cdot CO \cdot [CH_2]_3 \cdot CH(COMe) \cdot CONH_2$ .

This amide is most probably formed, together with its dehydro-derivative, when ethyl diacetylcaproate is treated with alcoholic ammonia as described above; but as the two compounds show great

similarity in their behaviour towards most solvents, they cannot easily be separated by fractional crystallisation. The amide is best prepared in a pure state by boiling the dehydro-compound for some time with water, separating the unchanged dehydrodiacetylcapronamide which crystallises from the solution on cooling, and allowing the solution to evaporate at the ordinary temperature. Diacetylcapronamide separates slowly in long, thick, transparent needles, or in flat, transparent, oblong plates containing 2 mols. of water of crystallisation. It loses its water when kept over sulphuric acid, and two determinations, made with different samples, gave the following results:—

I. 0.6219 gram of substance, dried between blotting-paper, lost 0.0944 gram over sulphuric acid.

II. 0.6195 gram substance, dried for a short time on a porous plate, lost 0.0995 gram over sulphuric acid.

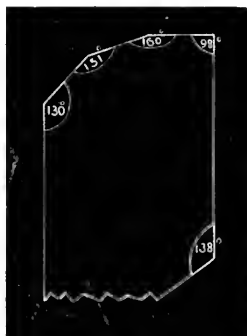
Calculated for $C_{10}H_{17}O_3N + 2H_2O$ .		Found.	
		I.	II.
$H_2O$ .....	15.3 p. c.	15.18	16.04 p. c.

The anhydrous substance was analysed and gave the following results:—

0.1744 gram substance gave 0.3871 gram  $CO_2$  and 0.1414 gram  $H_2O$ .

Calculated for $C_{10}H_{17}O_3N$ .		Found.	
C .....	60.30 per cent.	60.53 per cent.	
H .....	8.54 „	9.0 „	
N .....	7.03 „	—	

Diacetylcapronamide crystallises from dilute methyl alcohol in flat, transparent plates which effloresce, becoming opaque and very brittle



on exposure to the air. Some of these crystals were measured with a microscope provided with a graduated circle, and the observations made with one very well-defined crystal are given below.

Diacetylcapronamide has no well-defined melting point, as when heated to about  $200^\circ$  it begins to soften, and does not melt completely until  $228^\circ$ . It is readily soluble in cold methyl alcohol and in glacial acetic acid, but only moderately so in cold ethyl alcohol or water, and very sparingly in benzene, chloroform, ether, and acetone. It dissolves freely in warm, concentrated sulphuric acid, and is not precipitated when the solution is diluted; when boiled with soda, ammonia is evolved, and the characteristic smell of the compound  $C_9H_{14}O$  is perceptible.

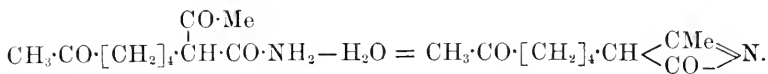
In studying the formation of dehydrodiacetylcapronamide from diacetylcapronamide, it is evident that the former substance may have either of the following formulæ:—

I.

II.

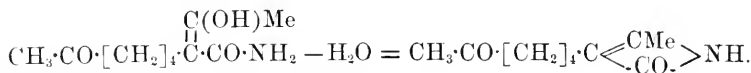


The formation of a substance represented by Formula I is easily understood from the following equation:—



Diacetylcapronamide.

In the case of Formula II it is necessary to suppose that diacetylcapronamide is first converted into its labile modification. The subsequent elimination of water taking place thus:—



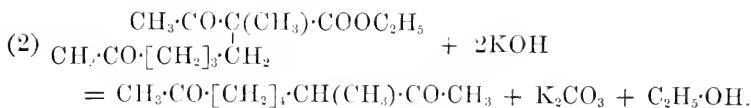
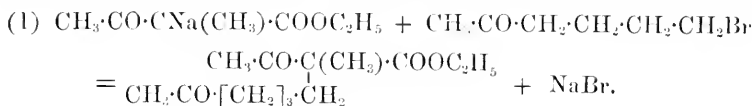
Diacetylcapronamide (labile form).

That Formula II represents the constitution of dehydrodiacetylcapronamide is proved by the fact that this substance yields an acetyl- and a nitroso-compound, and that on hydrolysis it is converted into diacetylcaproic acid.

The oily mother-liquors from which dehydrodiacetylcapronamide crystallises, were kept for a long time over sulphuric acid, but no further separation of crystals took place. The oil was therefore distilled under diminished pressure; considerable decomposition occurred, large quantities of ammonia and other gases being evolved, and a yellow oil collected in the receiver. The distillate was then

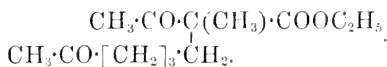
submitted to fractional distillation, but again considerable decomposition took place, and the resulting oily product seemed to consist of a mixture of several compounds, the separation of which has not yet been attempted.

In the course of our experiments on the behaviour of diacetylpentane towards dehydrating agents, a compound was obtained, the formation of which from the diketone might possibly be due to internal change in one of the  $-\text{CH}_2\cdot\text{CO}-$  groups. At an early stage of this investigation it was deemed important to prepare a diketone analogous to diacetylpentane in which methyl was substituted for one of the hydrogen atoms in one of the  $-\text{CH}_2\cdot\text{CO}-$  groups. Such a diketone should be obtained by treating the sodium compound of ethyl methylacetoacetate with acetobutyl bromide and hydrolysing the resulting ethyl  $\alpha$ -methyl- $\alpha\omega$ -diacetylcaproate; thus:



We append a brief account of the experiments which were carried out with this object.

*Ethyl  $\alpha$ -Methyl- $\alpha\omega$ -Diacetylcaproate,*



In preparing this substance, ethyl methylacetoacetate (32 grams) was gradually added to a cold solution of sodium (5.1 grams) in absolute alcohol (60 grams), acetobutyl bromide (40 grams) poured in, and the whole heated to boiling for about three hours. The alcohol was then distilled off, the residue mixed with water, and extracted several times with ether, the extract dried over calcium chloride, and the ether distilled off. The residual oil (57 grams) on fractioning under reduced pressure (220 mm.) separated into two portions boiling at  $109-205^\circ$  and  $205-270^\circ$  respectively. The higher boiling fraction was again distilled, and the portion boiling at  $255-260^\circ$  analysed with the following results:—

	Calculated for $C_{13}H_{22}O_4$ .	Found.
C . . . . .	64.46 per cent.	64.94 per cent.
H . . . . .	9.09 „	9.41 „
O . . . . .	26.45 „	25.65 „

Ethyl  $\alpha$ -methyl- $\alpha\omega$ -diacetylcaproate is a colourless oil possessing a faint odour. It is insoluble or nearly insoluble in water, but mixes with alcohol and ether in all proportions.

*$\alpha$ -Methyl- $\alpha\omega$ -Diacetyl-pentane*,  $CH_3 \cdot CO \cdot [CH_2]_4 \cdot CHMe \cdot CO \cdot CH_3$ .

In preparing this substance, 18 grams of the ethereal salt were mixed with a solution of 10 grams of pure potash in alcohol and heated for a short time on a water-bath. The decomposition set in almost immediately—much potassic carbonate separating out. After boiling for about an hour, the alcohol was distilled off, the residue mixed with water, and the alkaline product extracted two or three times with ether. The ethereal solution after drying over calcium chloride and evaporating, deposited a quantity of an almost colourless oil which on repeated distillation under diminished pressure (350 mm.), boiled fairly constantly at  $232$ — $235^\circ$ . This fraction was analysed with the following results:—

0.1705 gram substance gave 0.4400 gram  $CO_2$  and 0.1632 gram  $H_2O$ .

	Calculated for $C_{10}H_{18}O_2$ .	Found.
C . . . . .	70.59 per cent.	70.38 per cent.
H . . . . .	10.59 „	10.64 „
O . . . . .	18.82 „	18.98 „

$\alpha$ -Methyl- $\alpha\omega$ -diacetyl-pentane is a colourless, mobile oil, which even after long standing shows no signs of crystallisation; as it has frequently been noticed that methyl-derivatives of substances containing normal chains melt at a lower temperature than the substances themselves, methyldiacetyl-pentane might be expected to be an oil at the ordinary temperature. The diketone dissolves in a saturated solution of sodium hydrogen sulphite, and is reprecipitated on adding potassic carbonate, but no crystalline double compound was formed, as in the case of diacetyl-pentane.

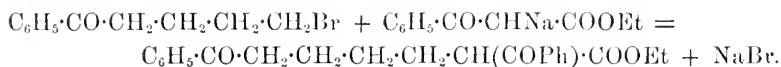
The alkaline solution, from which the diketone was separated by extraction with ether, contains considerable quantities of an oily acid, probably  $\alpha$ -methyl- $\omega$ -acetylcaproic acid.



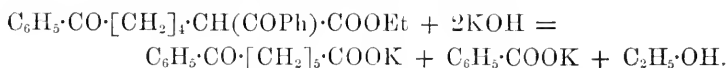
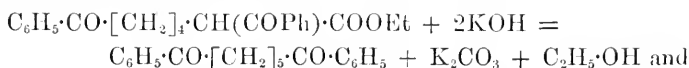
*Dibenzoylpentane.*

The results of experiments on the behaviour of diacetylpentane towards dehydrating agents made it necessary to determine whether either of the methyl-groups in this substance took part in the formation of the compound  $C_9H_{14}O$ , which has been referred to above. If a diketone analogous to diacetylpentane, but containing two phenyl-groups in place of the methyl radicles, was treated with dehydrating agents under the same conditions as those employed in the case of diacetylpentane, the results might be of considerable value in ascertaining the constitution of the compound  $C_9H_{14}O$ .

With this view we treated benzoylbutyl bromide with ethyl sodobenzoylacetate in alcoholic solution, and obtained ethyl  $\alpha\omega$ -dibenzoylcaproate, the reaction taking place in accordance with the equation—



When this ethereal salt is hydrolysed with alcoholic potash, it yields  $\alpha\omega$ -dibenzoylpentane, potassium  $\omega$ -benzoylcaproate, potassium benzoate, and potassium carbonate—



The benzoylbutyl bromide employed in these experiments was prepared by treating phenyldehydrohexone with concentrated hydrobromic acid, as has been previously described by one of us (Trans., 1887, 732). The crystalline product is dissolved in ether, the solution washed with dilute sodium carbonate solution until free from hydrobromic acid, dried over calcium chloride, and the ether evaporated. The benzoylbutyl bromide is thus obtained almost perfectly pure and quite colourless, and can be directly employed for the preparation of ethyl dibenzoylcaproate.

*Ethyl  $\alpha\omega$ -Dibenzoylcaproate*,  $C_6H_5 \cdot CO \cdot [CH_2]_4 \cdot CH(COPh) \cdot COOEt$ .

To a solution of 2.8 grams of sodium in absolute alcohol 24 grams of ethyl benzoylacetate are gradually added, care being taken to keep the temperature below  $40^\circ$ ; a slightly warm alcoholic solution of 28.8 grams of benzoylbutyl bromide is then poured in, and the

mixture heated on the water-bath with reflux condenser. Just as the alcohol begins to boil, the separation of sodium bromide commences, and after heating for about two hours the reaction is at an end. The alcohol is removed by distillation, the residue mixed with water, the product extracted with ether, and the ethereal solution dried and evaporated. Ethyl dibenzoylcaproate (about 42 grams) remains as a yellowish oil, and if the substances employed in the reaction are carefully weighed, the product is almost perfectly pure, as is shown by the following analysis, made with a sample which had been kept for a few days over sulphuric acid:—

0.1738 gram substance gave 0.4762 gram  $\text{CO}_2$  and 0.1112 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{22}\text{H}_{24}\text{O}_4$ .	Found.
C .....	75.0 per cent.	74.7 per cent.
H .....	6.8       ,,	7.1       ,,
O .....	18.2       ,,	18.2       ,,

It is a thick, yellowish oil, with an aromatic odour, and insoluble in water; even when kept for some weeks, it showed no signs of solidifying. When boiled with alcoholic potash, it is quickly hydrolysed and decomposed in accordance with the above equations.



This diketone is best prepared from the ethereal salt by a method similar to that employed in the preparation of diacetyl pentane. The crude ethyl dibenzoylcaproate (20 grams) is boiled for a short time with a solution of potash in methyl alcohol (= 10 grams KOH), this being added in small portions at a time as already described. The alcohol is distilled off, the residue treated with water to dissolve the sodium bromide, the oil extracted with ether, and the ethereal solution dried and evaporated. The diketone (14 grams) remains in the form of a thick, yellow oil, which quickly solidifies on cooling; after spreading on a porous plate to remove impurities, it was recrystallised from hot, dilute methyl alcohol, dried over sulphuric acid, and analysed.

0.1796 gram of substance gave 0.5347 gram  $\text{CO}_2$  and 0.1150 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{19}\text{H}_{20}\text{O}_2$ .	Found.
C .....	81.43 per cent.	81.20 per cent.
H .....	7.14       ,,	7.11       ,,
O .....	11.43       ,,	11.69       ,,

$\alpha\omega$ -Dibenzoylpentane crystallises from dilute methyl alcohol in long, colourless needles, melts at  $67-68^\circ$ , and when heated in small quantities under the ordinary pressure it distils at a temperature above  $300^\circ$  with only very slight decomposition. It is very readily soluble in cold acetone, but is precipitated in microscopic needles on adding water; it dissolves freely in cold benzene and ether, but is only moderately soluble in cold alcohol and seemingly insoluble in hot or cold water. It is readily soluble in warm, light petroleum ( $70-90^\circ$ ), and on cooling it separates from the solution almost completely in very slender needles.

Experiments on the behaviour of this diketone towards reducing and dehydrating agents are in progress.

*Dibenzoylpentanedioxime*,  $C_6H_5 \cdot C(NO_2) \cdot [CH_2]_3 \cdot C(NO_2) \cdot C_6H_5$ .

The dioxime was prepared by treating the diketone in alcoholic solution with hydroxylamine hydrochloride and a large excess of potash as recommended by Auwers (*Ber.*, **22**, 604). After keeping for two days the alcohol was distilled off, the residue mixed with water, and the solid substance which was precipitated separated by filtration and dried on a porous plate. It was then boiled with a small quantity of benzene to remove any unchanged diketone, the residue recrystallised from methyl alcohol, and dried at  $100^\circ$ . A nitrogen determination was made with the following result:—

0.1701 gram substance gave 13.4 c.c. of nitrogen measured at  $15^\circ$  and 736 mm.

	Calculated for $C_{19}H_{22}O_2N_2$ .	Found.
N .....	9.03 per cent.	9.23 per cent.

It crystallises from boiling methyl alcohol in small, glistening needles, melts at  $175-176^\circ$ , and is readily soluble in hot acetone and glacial acetic acid, but only very sparingly in boiling benzene, from which it separates in the form of a crystalline powder. It is very sparingly soluble in potash, but dissolves moderately easily in concentrated hydrochloric acid, yielding a colourless solution from which it is precipitated on adding water.

The alkaline filtrate from the dioxime, on acidifying with dilute sulphuric acid, gave a small quantity of a colourless substance which, after recrystallising from methyl alcohol, melted at  $168-169^\circ$  with previous softening, and consisted probably of slightly impure dioxime.

*$\omega$ -Benzoylcaproic Acid*,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot[\text{CH}_2]_5\cdot\text{COOH}$ .

The alkaline solutions from which  $\alpha\omega$ -dibenzoylpentane had been extracted as described above contain potassium  $\omega$ -benzoylcaproate and potassium benzoate. The free acids are precipitated on adding dilute sulphuric acid as an oil, which soon solidifies and can be separated by filtration. The quantity of the crude product obtained depends on the concentration of the alcoholic potash employed. In one experiment 20 grams of the ethereal salt was hydrolysed with an alcoholic solution of 10 grams of potash, and the crude acid mixture weighed 2 grams; in another experiment 40 grams of ethyl dibenzoylcaproate were treated with 40 grams of potash in methyl alcoholic solution and 12 grams of crude acids were obtained.

In order to remove the benzoic acid, the mixture (7 grams) is heated on a watch-glass at  $100^\circ$  until the weight becomes constant, which is the case after about 10 hours, and the residue (4.5 grams) recrystallised twice from light petroleum. The pure compound melted at  $81\text{--}82^\circ$ , and gave the following results on analysis:—

0.1449 gram substance gave 0.3773 gram  $\text{CO}_2$  and 0.0986 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{13}\text{H}_{16}\text{O}_3$ .	Found.
C .....	70.90 per cent.	71.01 per cent.
H .....	7.27 „	7.56 „
O .....	21.83 „	21.43 „

$\omega$ -Benzoylcaproic acid crystallises from boiling light petroleum in long, glistening, transparent, plates and from boiling water, in which it is only sparingly soluble, in slender, microscopic needles. It is very readily soluble in cold methyl alcohol, ethyl alcohol, ethyl acetate, and benzene, but only moderately soluble in boiling light petroleum, and almost insoluble in the cold.

The *silver* salt was prepared by precipitating a neutral, aqueous solution of the ammonium salt with silver nitrate, washing the precipitate with cold water, and drying over sulphuric acid. Analysis:—

0.3604 gram of the salt gave 0.1186 gram of silver.

	Calculated for $\text{C}_{13}\text{H}_{15}\text{O}_3\text{Ag}$ .	Found.
Ag .....	32.97 per cent.	32.91 per cent.

is a colourless, seemingly amorphous compound, very sparingly soluble in boiling water, which does not darken on exposure to light; when heated, it turns a beautiful peacock-green.

The *cadmium* salt, prepared by treating an aqueous solution of the ammonium salt with cadmium chloride, separates from hot water in colourless microscopic needles. Mercuric nitrate produces in aqueous solutions of the ammonium salt a colourless, flocculent precipitate which is soluble in boiling water. Lead acetate gives a white, amorphous precipitate, copper sulphate a bluish-green precipitate, and ferric chloride a flesh-coloured precipitate. The barium salt and the calcium salt are granular, crystalline compounds readily soluble in hot water.

*Oxime of  $\omega$ -Benzoylcaproic Acid*,  $C_6H_5 \cdot C(NO \cdot H) \cdot [CH_2]_5 \cdot COOH$ .

$\omega$ -Benzoylcaproic acid, dissolved in alcohol, was treated with hydroxylamine hydrochloride and a large excess of potash, and the solution kept for two days at the ordinary temperature. The alcohol was then partially distilled, the residue mixed with water, acidified with dilute hydrochloric acid, and the precipitated oil extracted with ether; the ethereal solution was washed once or twice with dilute hydrochloric acid, and then with water, dried, and the ether evaporated. The oxime remained as a yellowish oil, which, when kept over sulphuric acid under diminished pressure, gradually solidified. It was spread on a porous plate, washed with a little light petroleum, dissolved in cold benzene, and precipitated from the solution with light petroleum.

The oxime of benzoylcaproic acid is thus obtained in colourless, microscopic needles melting at about  $75^\circ$ . A nitrogen determination gave the following results:—

0.1996 gram substance gave 10.25 c.c. N at  $14^\circ$  and 740 mm.

	Calculated for $C_{13}H_{17}O_3N$ .	Found.
N .....	5.96 per cent.	5.88 per cent.

It is very readily soluble in ether and cold benzene, but only sparingly in hot water, and almost insoluble in cold light petroleum. It dissolves freely in caustic alkalis and in concentrated hydrochloric acid, but it is partially reprecipitated when the acid solution is diluted.

XXXVIII.—*Acetopropyl Alcohol and Acetobutyl Alcohol.*

By HAROLD G. COLMAN, M.Sc., Ph.D., and W. H. PERKIN, Junr.

IN a previous communication to the Society (Trans., 1887, **51**, 702), it was shown by one of us that acetobutyl alcohol, obtained by boiling methyldehydrohexonecarboxylic acid with water, differs very widely from the substance of that name obtained by Lipp (*Ber.*, 1885, 3280) by boiling ethylic  $\alpha$ -bromopropylacetoacetate with dilute hydrochloric acid, the boiling point of the former being  $227^{\circ}$ , whereas the latter product distilled at  $154$ – $155^{\circ}$ , a difference of  $70^{\circ}$ .

In a paper published some time since (*Ber.*, 1888, 2138), "On the Action of Sodium on Ethylic Monochloracetate," Fittig and Erlenbach, in describing a substance boiling at  $128^{\circ}$ , which they supposed to be acetoisopropyl alcohol, took occasion to state that the acetobutyl and acetopropyl alcohols previously described by us could not possibly have the constitution assigned to them—owing to their syrupy consistency and high boiling points—and that the description given by Lipp of his acetobutyl alcohol agreed much better with the properties such a substance might be expected to possess. In a later paper (*Ber.*, 1888, 2647), these chemists discovered that their compound was not acetoisopropyl alcohol, but was simply acetol ethyl ether,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_2\text{H}_5$ .

As, however, in spite of this, they did not withdraw their previous remarks on the nature of acetopropyl and acetobutyl alcohols, and as we have extensively used these substances in the synthesis of ring-derivatives, and drawn important theoretical conclusions from the results obtained, we have thought it necessary to again carefully examine these alcohols with a view to further establishing their identity.

If the question of the probable properties of such a substance as acetobutyl alcohol,  $\text{CH}_3\cdot\text{CO}\cdot[\text{CH}_2]_3\cdot\text{CH}_2\cdot\text{OH}$ , is carefully examined, it is soon apparent that a compound of this formula should be a thick oil boiling considerably above  $200^{\circ}$ .

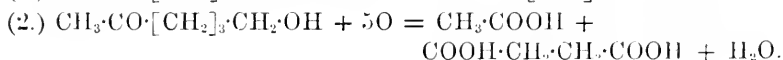
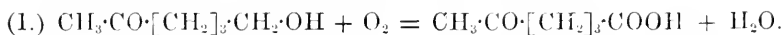
Taking into account a large number of cases, it is found that the usual result of displacing one hydrogen-atom in an organic substance (boiling between  $100^{\circ}$  and  $130^{\circ}$ ) by the group  $\text{CH}_3\cdot\text{CO}$ , is to raise the boiling point of that substance some  $100^{\circ}$  to  $120^{\circ}$ .

Now, taking normal butyl alcohol (b. p.  $118^{\circ}$ ) as a basis, and substituting  $\text{CH}_3\cdot\text{CO}$  for one hydrogen-atom, we find that the calculated boiling point of acetobutyl alcohol lies between  $218^{\circ}$  and  $238^{\circ}$ , whilst the boiling point observed was  $227^{\circ}$ . Again, acetobutyl alco-

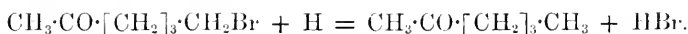
hol would, in its physical properties, bear considerable resemblance to the class of glycols, and this is borne out by the fact that these compounds, and particularly the higher numbers, are thick, oily liquids boiling at high temperatures.

In the original investigation of acetobutyl alcohol (Trans., 1887, **51**, 717—725) the following attempts were made to prove its constitution.

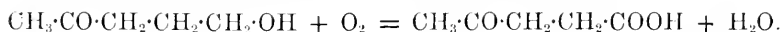
The ketonic nature of the substance was demonstrated by the fact that it combined with phenylhydrazine—the fact that it was also an alcohol was shown by its being converted into acetobutyl bromide on treatment with aqueous hydrobromic acid. The portion of the carbonyl-group in relation to the alcohol-group was shown by the behaviour of acetobutyl alcohol on oxidation, when it decomposed first into acetobutyric acid and then, under the influence of an excess of oxidising agent, into acetic acid and succinic acid:—



The constitution of acetobutyl alcohol is also clearly demonstrated by the reduction of acetobutyl bromide to methyl butyl ketone by means of zinc and acetic acid:—



The constitution of acetopropyl alcohol was proved by the fact that this substance on oxidation yields levulinic acid, thus:—



Fittig, however, does not consider this a proof of the constitution of this alcohol (*Ber.*, **21**, 2139).

In order, if possible, to bring further proof of the constitution of these two important ketone alcohols, specimens of each were prepared and purified with the greatest care, and their magnetic rotation determined by Dr. W. H. Perkin, senr. The numbers obtained showed clearly that these substances had the constitution assigned to them, and that they were two members of a homologous series, the difference for  $\text{CH}_2$  being found as 0.958 instead of 1.023.

These proofs of the constitution of the acetopropyl and acetobutyl alcohols being so satisfactory, all that remained to be done was to examine into the nature of the substance described by Lipp as acetobutyl alcohol, and to determine in what respects this substance differed from the acetobutyl alcohol obtained by boiling methyl-dehydrohexanecarboxylic acid with water.

The hydrolysis of ethylic  $\alpha$ -propylacetoacetate by means of hydrochloric acid was therefore carried out according to Lipp's directions, and as a result an oil was obtained which, on analysis, gave numbers agreeing approximately with those required for acetobutyl alcohol, and which distilled apparently at 154—155°. Subsequent experiments showed, however, that this temperature, instead of being the boiling point, was in reality the decomposing point of the alcohol: the reason for this being, that the slightest trace of impurity is sufficient to prevent acetobutyl alcohol from distilling without the most rapid decomposition into its anhydride (methyldehydrohexone) and water, the thermometer remaining constant at 154—155°.

Lipp's acetobutyl alcohol, when not too impure, can be distilled with slight decomposition under reduced pressure; the boiling point noticed in two cases being 157° under 100 mm. pressure and 171° under 177 mm. pressure; on distilling acetobutyl alcohol from methyldehydrohexonecarboxylic acid under the same conditions, almost identical boiling points were noticed.

Pure acetobutyl alcohol was obtained from Lipp's crude product by distilling with steam, fractioning the methyldehydrohexone thus obtained, and treating it with water. In this way a thick oil was obtained which distilled under ordinary pressure at 225—227°, and was in every respect identical with the acetobutyl alcohol from methyldehydrohexonecarboxylic acid.

These and other experiments, an account of which will be given later on, prove conclusively that acetobutyl alcohol when pure boils at 225—227°, and not at 154—155° as stated by Lipp. Acetopropyl alcohol behaves in every respect, physically as well as chemically, as the lower homologue of acetobutyl alcohol, and as this substance gives levulinic acid on oxidation, no further experiments in proof of its constitution are necessary.

#### *Preparation of Acetobutyl Alcohol by Lipp's Method.*

In repeating Lipp's experiments, his instructions, as given in the *Berichte*, 18, 3275, were followed exactly, with the one exception that instead of 80 grams of trimethylene bromide 50 only were taken, the former number being evidently a misprint, as is clearly seen from the fact that Lipp mentions that he uses 1 mol. of trimethylene bromide to 1 mol. of ethylic sodacetoacetate.

The oil obtained by the addition of water to the product of the reaction was washed with caustic potash solution, and then with water, and dried over potassic carbonate. This crude ethylic bromopropyl acetoacetate weighed from 55 to 60 grams; it contained as impurity considerable quantities of trimethylene bromide and some



ethyl methyldehydrohexonecarboxylate, besides small quantities of ethylic acetoacetate. This oil was now digested with hydrochloric acid, the same quantities being used as given by Lipp, the product separated from the unchanged trimethylene bromide (about 20 grams), and about one-fifth of the water distilled off. The solution was then saturated with potassic carbonate, and the oily layer which separated dried over potassic carbonate, and allowed to stand for three or four days over sulphuric acid in a vacuum as Lipp directs, and then analysed.

Two different samples gave the following numbers:—

- I. 0.1545 gram substance gave 0.1390 gram  $\text{H}_2\text{O}$  and 0.3380 gram  $\text{CO}_2$ .
- II. 0.2340 gram substance gave 0.2090 gram  $\text{H}_2\text{O}$  and 0.5150 gram  $\text{CO}_2$ .

	Calculated for $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ .	Found.	
		I.	II.
C . . . . .	62.06 p. c.	59.67	60.02 p. c.
H . . . . .	10.35 „	10.00	9.92 „
O . . . . .	27.59 „	30.33	30.06 „

An examination of this oil showed that it contained, besides other impurities, small quantities of bromine. On submitting it to fractional distillation under the ordinary pressure, the thermometer rises rapidly to  $150^\circ$ , at which temperature vigorous decomposition sets in, and between  $150$ — $160^\circ$  almost the whole distils over, the distillate consisting of two layers, the upper one being a mixture of methyldehydrohexone with acetobutyl alcohol, and the lower one acetobutyl alcohol and water. The boiling point,  $154$ — $155^\circ$  (718 mm.), given by Lipp is, therefore, evidently the decomposition point of this crude alcohol into water and its anhydride methyldehydrohexone. These recombine to some extent in the receiver, and probably almost entirely on standing.

A very carefully prepared sample of Lipp's product was now fractioned under reduced pressure (100 mm.), when it was found to boil fairly constantly at  $157^\circ$  with very little decomposition. An analysis of this preparation gave the following result:—

- 0.1335 gram substance gave 0.1260 gram  $\text{H}_2\text{O}$  and 0.3015 gram  $\text{CO}_2$ .

	Calculated for $\text{C}_6\text{H}_{12}\text{O}_2$ .	Found.	
C . . . . .	62.06 per cent.	61.59	per cent.
H . . . . .	10.35 „	10.49	„
O . . . . .	27.59 „	27.92	„

Even after distillation in a vacuum, this alcohol is far from pure, and attempts to refraction the product invariably lead to its decomposing into anhydride and water even under very low pressures such as 20—30 mm., and, curiously enough, although this substance was prepared a great number of times, it was only on two occasions found possible to distil it at all.

An attempt was next made to purify this crude substance by distillation in a current of steam. About 30 grams of the crude oil were taken, and the distillate containing a quantity of oil in suspension was extracted with ether. The ethereal solution was dried carefully over carbonate of potash, the ether distilled off, and the resulting oil distilled. Almost the whole passed over between 105° and 111°, and on re-fractioning a beautifully colourless oil was obtained boiling constantly at 109°, and consisting of pure methyldehydrohexone, as the following analysis shows:—

0.2100 gram substance gave 0.1947 gram H<sub>2</sub>O and 0.5638 gram CO<sub>2</sub>.

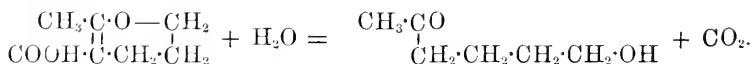
	Calculated for C <sub>6</sub> H <sub>10</sub> O.	Found.
C .....	73.46 per cent.	73.21 per cent.
H .....	10.20 „	10.29 „
O .....	16.33 „	16.50 „

When shaken with a considerable quantity of distilled water and allowed to stand for some days, this oil completely dissolves forming acetobutyl alcohol. On saturating the solution with carbonate of potash, extracting with ether, drying very thoroughly over carbonate of potash, and evaporating, a colourless oil was obtained which under the ordinary pressure distilled without decomposition between 225—227°, and gave the following numbers on analysis, showing that it was pure acetobutyl alcohol.

0.1604 gram substance gave 0.1538 gram H<sub>2</sub>O and 0.3657 gram CO<sub>2</sub>.

	Calculated for C <sub>6</sub> H <sub>12</sub> O <sub>2</sub> .	Found.
C .....	62.06 per cent.	62.17 per cent.
H .....	10.35 „	10.65 „
O .....	27.59 „	27.18 „

On careful examination, this substance was found to be identical in all respects with the acetobutyl alcohol previously obtained by one of us (*Trans.*, **51**, 716—720) by boiling methyldehydrohexonecarboxylic acid with water—



The decomposition represented by this equation is not only a quantitative one, but the acetobutyl alcohol obtained is so pure that when perfectly dry it distils at once at  $227^{\circ}$  with the merest trace of decomposition, the resulting product being almost free from smell.

The camphoric odour which Lipp ascribes to his product is due to various impurities, and particularly to methyldehydrohexone, the presence of this substance would also explain the mobility of Lipp's alcohol.

*Acetopropyl Alcohol*,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ , and *Acetopropyl Bromide*,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$ .

The acetopropyl alcohol used in the following experiments was prepared according to a method previously described (Trans., 1887, 51, 829), which consists in boiling acetyltrimethylenecarboxylic acid with water until the evolution of carbon dioxide ceased, saturating the liquid with potassic carbonate, and extracting with ether. The product obtained boiled constantly at  $144\text{--}145^{\circ}$  (100 mm.), and possessed all the properties previously assigned to it.

To prepare acetopropyl bromide, the alcohol was mixed with a saturated aqueous solution of hydrogen bromide, and the liquid heated on a water-bath for one hour. The product was poured into water, the excess of hydrogen bromide neutralised with sodic carbonate, and the bromide repeatedly extracted with ether, the ethereal solution evaporated, and the resulting oil fractioned under a pressure of 90 mm. Almost the whole of it distilled at  $115\text{--}120^{\circ}$ , a little hydrogen bromide being eliminated, as is also the case in the distillation of acetobutyl bromide; owing to this decomposition, the bromine determinations made with a product boiling constantly at  $118^{\circ}$  (90 mm.) came a little too low.

I. 0.1548 gram substance gave 0.1687 gram AgBr.

II. 0.1807 gram substance gave 0.1973 gram AgBr.

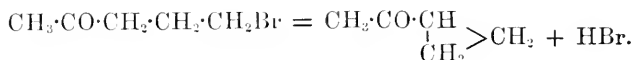
III. 0.2350 gram substance gave 0.2480 gram AgBr and 0.0050 gram Ag.

Calculated for		Found.		
$\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$ .		I.	II.	III.
Br . . . . .	48.48 p. c.	46.37	46.42	46.48 p. c.

When freshly distilled, acetopropyl bromide is a colourless mobile liquid, which has a penetrating odour closely resembling that of acetobutyl bromide. On standing, it rapidly becomes dark coloured, especially when acted on by light.

Acetopropyl bromide is remarkable for the ease with which it decomposes with elimination of hydrogen bromide. Experiments

made on the action of sodic ethylate and ethylic sodiomalonate on this bromide invariably resulted in the formation of a light, ethereal oil boiling at  $113^{\circ}$ , which appears to be identical with acetyltrimethylene (Trans., 1887, **51**, 832). In that case, it would seem that the elimination of hydrogen bromide took place according to the equation—



As we were on the point of forwarding this paper for publication, we received the last number of the *Berichte*, containing an article by Lipp on acetopropyl alcohol (*Ber.*, **22**, 1196).

In this article Lipp describes a repetition of the experiments made some time since by Freer and Perkin (Trans., 1887, **51**, 834—835) on the action of hydrogen chloride on ethylic  $\omega$ -bromethylacetoacetate, his results confirming in every particular those previously obtained. On account of the comparatively high temperature at which acetopropyl alcohol boils, Lipp states in a footnote (p. 1198) that the boiling point of acetobutyl alcohol previously given by him, is probably the decomposition point of this substance, a view which agrees with that deduced by us from the results of the experiments described in our present paper. Lipp then proceeds to describe the preparation of acetopropyl alcohol by the hydrolysis of the crude product of the action of ethylene bromide on ethylic sodacetoacetate (ethylic  $\omega$ -bromethylacetoacetate), and gives in detail the conversion of this alcohol into levulinic acid by oxidation. These reactions have already been carefully studied by Freer and Perkin (Trans., 1887, **51**, 834) and by Colman and Perkin (1888, **53**, 189—190). Lipp also prepared  $\omega$ -bromopropyl methyl ketone (acetopropyl bromide) by treating acetopropyl alcohol with hydrogen bromide, and his description of this substance agrees in every respect with that given by us in this paper.

In this interesting paper on acetobutyl alcohol, Lipp has unfortunately based his criticisms of the results previously obtained by us on short and very incomplete abstracts of our papers which have from time to time appeared in the *Chemisches Centralblatt*, and he has thus been led to make a number of experiments which otherwise would have been unnecessary.

To this cause is also to be attributed the statement that he makes that we never prepared acetopropylalcohol in a pure condition, and that we obtained it only as a very thick, unstable oil, which decomposed on distillation. On referring to our original papers (*loc. cit.*), it will be found that every pains was taken to get this substance in an especially pure condition, in order to allow of its magnetic rotation being deter-

mined, and, as a result, a beautiful product was obtained, boiling constantly at 144—145° (100 mm. pressure), and this, as the analytical numbers, as well as those obtained in the determination of its magnetic rotation show, must have been very pure indeed. Both acetopropyl alcohol and acetobutyl alcohol have been prepared by us in very large quantities for use in various synthetical experiments, and experience has shown that these substances are very readily obtained in a state of purity by boiling acetyltrimethylene- and methyldehydrohexone-carboxylic acids with water, whereas the products obtained by the hydrolysis of ethylic  $\omega$ -bromethyl- and bromopropyl-acetoacetates are invariably very crude and difficult to purify. A criticism of the remarks which Lipp makes, at the conclusion of his article, as to the constitution of ethylic acetyltrimethylene carboxylate, will form the subject of a future paper.

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### XXXIX.—*An Improved Soxhlet Extractor, and Apparatus for Distilling in a Vacuum.*

By J. LEWKOWITSCH, Ph.D.

#### (1.) *An Improved Soxhlet Extractor.*

WHEN using the ordinary form of Soxhlet extractor, there is always a doubt as to the exact time when the substance is completely extracted, unless the whole apparatus is taken to pieces, and a test made by putting a fresh supply of the solvent into the extractor. As a rule, therefore, the extraction lasts far longer than is necessary, and this involves not only loss of time but also of the volatile solvent. To avoid this, I use a Soxhlet extractor, fitted up with a test tap in the syphon-tube as shown in Fig. 1; this allows a few drops of the solvent to be drawn off at any time to see whether it contains any of the substance to be extracted.

#### (2.) *Flask for Distilling Frothing Liquids in a Vacuum.*

On distilling frothing liquids in a vacuum, it has always been found useful to allow a very small quantity of air or of an indifferent gas to pass through the liquid by means of a finely-drawn tube, reaching nearly the bottom of the distilling-flask. When the quantity of the substance is small, and a small distilling-flask has to be

used, it will be found almost impossible to insert at the same time both a tube of this kind and a thermometer. In this case, I find a distilling-flask of the form of Fig. 2 very convenient.

FIG. 1.

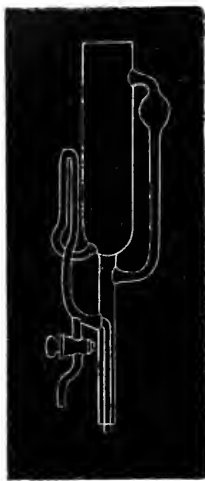
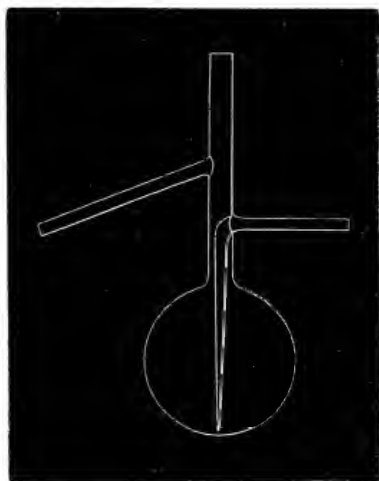


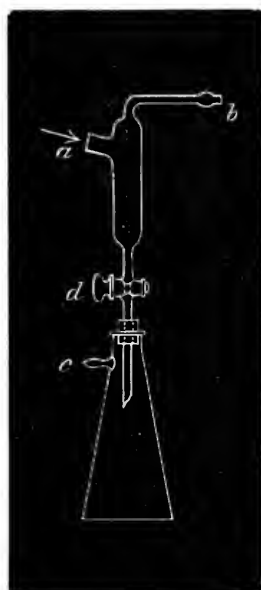
FIG. 2.



(3.) *An Adapter for Fractional Distillation in a Vacuum.*

Numerous pieces of apparatus for this purpose have lately been described, most of which are very complicated, and, therefore, out of the question in a laboratory, where fractional distillation in a vacuum has to be performed daily. I recommend, therefore, in cases where a vacuum-pipe with several taps is available (or a second water injector-pump) an adapter like that shown in Fig. 3. The tube *a* is connected with a Liebig condenser, and *b* and *c*, by means of india-rubber tubing, with two taps of the vacuum-pipe. On starting, the distilling-flask, the adapter and the Erlenmeyer flask are exhausted through *b* and *c*, the stopcock *d* being open. When the first fraction is collected, the tap *d* is closed, whereby the Erlenmeyer flask is shut off from the vacuum-pipe *b*, and it is then filled with air by disconnecting the india-rubber tubing from *c*. The Erlenmeyer flask can now easily be taken off, and emptied or replaced by another, while the distillation is carried on without interruption. When the Erlenmeyer flask is fitted on again, it is exhausted at *c* as before, the tap *d* opened, and the second fraction collected. I have used this adapter for some years, and found it work most satisfactorily.

FIG. 3.



XI.—*On a Method of Investigating the Dissolution of Metals in Acids.*

By V. H. VELEY, M.A., the University Museum, Oxford.

*Introduction.*

IN recent years, various accounts have been published on the dissolution of metals in acids as a result of a chemical change. Thus Kajander in *Bull. Soc. Chim.* [2], 34, 325 (an abstract from a Russian communication), has determined the relation between the weights of magnesium dissolved per unit time, and the concentration of the acids used, as also the variation produced by the addition to the acid of foreign salts and liquids. Thorpe (*Trans.*, 1882, 287) has studied the reduction of ferric salts in acid solutions by various metals. Divers (*Trans.*, 1885, 598) has ascertained the relative effects of sulphuric and nitric acids, taken separately and together on metallic zinc. More recently, Spring and van Aubel (*Ann. Chim. Phys.* [6],

11, 505) conducted some elaborate experiments on the interaction of zinc, containing a small proportion of lead, with sulphuric and the halogen acids. In most of the experiments described in these memoirs, a more or less regular surface of the metal has been placed at rest within the dissolving acid, and either the loss in weight of the metal determined at given intervals or the times noted which were required for the evolution of a definite volume of hydrogen or other gas. From these experiments the observations of those familiar with the preparation of hydrogen from zinc and sulphuric acid have been confirmed, namely, that within certain limits the more concentrated the acid and the higher the temperature, the more rapid the solution\* of the zinc. But in the method of experiment adopted the measured result is one of mixed causes, each one of which is variable at any moment of time, and its peculiar effect not susceptible of mathematical analysis. For it is obvious that if the metal is *at rest* within the acid its measured rate of solution is dependent, *inter alia*, not only upon the surface exposed and the local rise of temperature due to the chemical reaction, but also upon the rate of diffusion of the metallic salt formed in the acid liquid, the actual disengagement of the gas-bubbles from the surface of the metal, and the rate of removal by these bubbles of the concentrated salt solution in the immediate vicinity of the metal. Thus if a cylinder of zinc be placed in dilute sulphuric acid, it is a common matter of observation that at first the bubbles of hydrogen gas persistently cling to the metallic surface, but subsequently are more readily removed owing to the formation of points on the surface due to the production of local electric circuits. In another paper (*Phil. Trans.*, 1888, A, 285), I have remarked that the increase in the rate of evolution of hydrogen from zinc and dilute sulphuric acid caused by the reduction of the superincumbent pressure, can partly be explained by the formation of larger bubbles of gas, whereby the solution of the zinc sulphate is more readily removed. Again, though as is well known, zinc under the same conditions dissolves more readily in dilute hydrochloric than in sulphuric acid containing the same quantity of replaceable hydrogen per unit volume, yet it is possible that this result may be due to the greater diffusibility of zinc chloride in hydrochloric acid than of zinc sulphate in sulphuric acid. Spring and van Aubel in their experiments either kept the surface of the metal constant or allowed for its variation, but the results of others, obtained with sheets of metal, are comparatively valueless in that the actual surface owing to inequalities may vary within almost infinite limits. To

\* Here and throughout this paper the word "*solution*" will be used, it being understood to imply solution *as a result of chemical change*, between the metal and the acid.

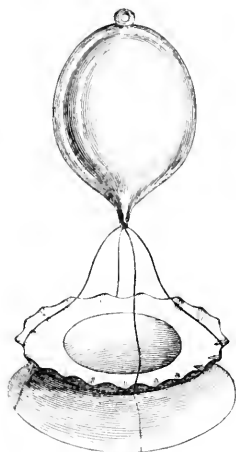


avoid some of the above difficulties, attempts were made to devise a method which could be applied to measure the rate of solution of metals in acids under such conditions that not only fresh surfaces of a regular geometric figure of the metal are continually being exposed, but also the products of the change, whether gas or metallic salt, are continually being removed from the vicinity of the dissolving metal. An outline of the research has already been indicated in this Journal (Abstr., 1888, 104).

### *Apparatus.*

The first apparatus used consisted of two watch-glasses (Fig. 1) placed one above the other in opposite positions, so that the upper one presented from above a concave, the lower a convex surface. These

FIG. 1.



glasses were wired to one another, as also to a hollow glass bulb by means of which they were floated under the surface of the acid liquid contained in a beaker. The liquid was kept stirred by a current of carbonic acid produced in a Kipp's apparatus and washed by bubbling through a Wolff's bottle containing water; thence it passed into a piece of quill glass tubing bent twice at right angles, and ending in a small thistle-funnel. The horizontal and lower vertical limb of the tube were of such lengths and the containing beaker of such a dimension that each bubble of the gas as it issued from the thistle-funnel struck the lower of the two watch-glasses on one side, and thus in passing by tilted the whole arrangement of glasses and bulb. The

down-draught of the liquid caused the apparatus to return to its former position in time for another gas-bubble to tilt it again. Thus the whole of the acid liquid was continually stirred, and a spherical bullet of metal on the upper of the two watch-glasses continually rolled about.

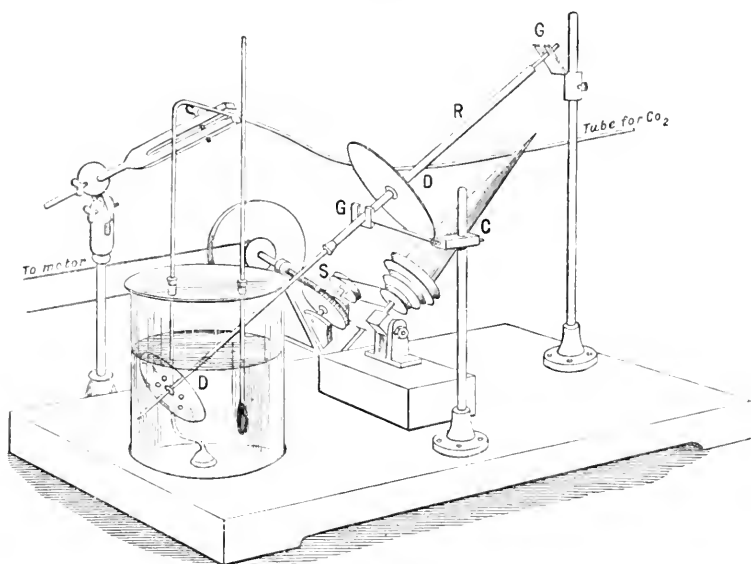
The edge of the upper glass was slightly corrugated, so that the bullet should not roll off. The friction between the glass and bullet, together with a slight spin given by the gas-bubbles, prevented the bullet from rolling always on the same axis, and thus become spheroidal. This apparatus was devised some years ago by Mr. Vernon-Harcourt for experiments on the same subject.

The beaker was placed on an iron plate, under which was a small gas-flame; the variations of temperature did not exceed a few tenths of a degree on either side of that required. To prevent access of dust the beaker was covered with a glass plate provided with two holes, through one of which passed the thermometer, through the other the carbonic anhydride tube. Experience showed that it was above all things necessary to pass the same number of gas-bubbles per minute.

The apparatus described above, though simple, yet presented some disadvantages. Firstly, it is obvious that, assuming the impact given by each bubble of carbonic anhydride to be equal, a smaller bullet would receive a greater shock than a larger one, and as all experiments showed that the rate of solution, *ceteris paribus*, varied with the motion imparted to the bullet, the amount dissolved per unit area would increase with decrease of its size. This was found to be the case after a certain limit had been passed. Secondly, it was found difficult in practice to ensure the passage of the same number of gas-bubbles per minute. The results, however, obtained with the apparatus were sufficiently accurate to determine the relation between the rate of solution and the temperature, and are recorded below in Tables I to X. To obviate this source of error and inconvenience an integrating machine was devised, by means of which the bullet was caused to revolve round the same path the same number of times, whatever its diameter. The apparatus consisted essentially of a wooden cone C (Fig. 2), rotated by means of a water-motor; a brass disc, D, worked by friction on the cone, and the former could be moved along a brass rod, R, provided with a scale of 200 mm., and set parallel to the cone; the rod rested above and below upon guides, G, G', screwed to a wooden base-board. The lower extremity of the rod ended in a hollow ferrule, into which was inserted a rubber cork; through this passed a sealed piece of glass tubing, bearing at a convenient distance from the end of the rod, a small flat glass dish, D, about 70 mm. in diameter, with upturned edges. The dish was

pierced with several holes to allow the liquid to flow out continually. The tube and dish were set at angle of  $45^\circ$  within the beaker contain-

FIG. 2.



ing the dissolving liquid; the metallic bullet rested on the rim of the dish.

When the cone is rotated at a uniform rate, the rotation of the brass rod, as also of the glass vessel, varies with the position of the disc on the cone; accordingly, for any known diameter of the bullet the disc is placed at a certain mark on the graduated scale of the brass rod. Thus, the rotation of the rod and of the dish can be made proportional to the diameter of the bullet, so that it will be revolved round the same path the same number of times, whatever be its diameter. The glass dish was set slightly eccentrically on the tube to prevent the bullet from always revolving on the same axis. To reduce the velocity of the rotation of the water-motor, the driving wheel of which revolved about 1560 times per minute, a tangent screw (S) was interposed between it and the cone; the rotation of a driving wheel connected with the screw was kept constant at 26 times per minute, whereby the rotation of the cone, worked by an endless band, was also kept constant. This apparatus was devised in outline by my friend Mr. V. P. Sells, of New College, Oxford (to whom I would express my thanks); it was constructed and improved by the

Cambridge Philosophical Instrument Company. The results obtained by its use are recorded in Tables XI to XXI. In these latter experiments, a fairly uniform current of carbonic anhydride was passed as before, and the arrangements for keeping the temperature constant (not represented in cut) were slightly modified.

*Determination of the Surfaces of the Bullets.*

If it could be insured that a metallic bullet, initially spherical, retained its form perfectly, its surface could be calculated from its mass and specific gravity. As, however, this was not always the case, it was thought to be more exact to calculate the area from a measurement of the axes taken in different directions; this was effected by means of a micrometer caliper, which measured to 0.013 mm.

The areas corresponding to each of the several diameters were calculated, and their mean value  $A_1$  taken. After the bullet had been rolled about in the acid liquid for one hour, it was removed, washed with distilled water, and dried at 80—90°; its axes were again measured, their corresponding areas calculated, and their mean value  $A_2$  taken. The average of the former and latter mean values, namely,

$\frac{A_1 + A_2}{2} = A$ , was taken as the mean area of the bullet during the course of the experiment. The difference between the greatest and least axis seldom exceeded 0.05 mm. (the difference being generally 0.026 mm.); when, however, this was the case, the area was calculated by means of the following approximate formula:—Let  $2a, 2b, 2c$

be the greatest, mean, and least axis respectively, and let  $e$  be the eccentricity of the  $ab$  section ellipse given by (i)  $b^2 = a^2 (1 - e_1^2)$ , and  $e^2$  that of the  $bc$  section ellipse given by (ii)  $c^2 = b^2 (1 - e_2^2)$ . Then total surface of the ellipsoid,  $e_1$  and  $e_2$ , being very small;

$$(iii) \ A = 4\pi C^2 \left(1 - \frac{e_1^2 - e_2^2}{3}\right),$$

wherein  $e_1$  and  $e_2$  are given by (i) and (ii).

*Method of Experiments.*

The bullet was weighed before and after each experiment, and the loss in weight  $M$ , divided by the mean area  $A$ , was taken as the factor for the comparison of the results. For convenience this is expressed in terms of decimilligrams dissolved per one square millimetre surface. To make clear the whole course of the experiments, all the measurements and weighings are given below in Table I(a) and (b).

Throughout the various manipulations, the metallic bullet was never touched by the fingers, but only with a pair of brass pincettes,

as it is well known that the presence of a trace of grease materially affects the rate of solution of metals in acids.

In the first series of experiments, such metals and acid solutions were used that no gas was evolved as such, as for example, zinc and copper in chromic acid (potassium bichromate and sulphuric acid). As the results with pure redistilled zinc were rather irregular, pure electrotype copper was used. Messrs. Johnson and Matthey made from my instructions a set of copper bullets from one rod cast from the purest electrotype copper, each bullet weighing about 5 grams and turned to 0.013 mm. Before any measurements and weighings were made the bullets were rolled about in a solution of chromic acid of similar strength to that used in the actual experiments. By this means any polishing material used by the workmen, as also any superficial coating of oxide were removed, so that the bullet at the commencement of the first experiment presented a surface similar to that in all the subsequent experiments. It was invariably found that this exterior coating was much less readily dissolved off than the remainder; this was doubtless due to a denser structure of the metal produced by the external pressure to which the bullets were subjected in the processes of turning and polishing. The same result was produced in a more exaggerated degree by heating the bullets for some time at a temperature just short of that at which they softened, and subsequently allowing them to cool slowly. In this preliminary operation about 0.25 gram was removed. After the copper bullets had been in the chromic acid solution for several hours, their surfaces were, with few exceptions, as smooth and regular as at the start; the absence of any irregularities was at least one criterion of the homogeneity of the copper.

For each separate experiment, a solution of potassium bichromate was made by dissolving a known weight of the crystals in water; to it was added a volume of diluted sulphuric acid containing a known weight of the acid; the whole was then made up to one litre. The strength of the sulphuric acid, a considerable quantity of which was made up at one time, was determined either by precipitation with barium chloride, or by titration with sodium carbonate. In the first series of experiments, such quantities of potassium bichromate were used that taking the average quantity 0.33 gram of copper dissolved off in each experiment, the quantities of bichromate and acid should each be diminished by about 2 per cent. with formation of 0.2 per cent. of water, if the action is supposed to be expressed by the following equation:—



Thus if 59 grams of the bichromate and 64.4 grams of sulphuric

acid are taken, 2.0 per cent. of the former acid and 2.1 per cent. of the latter are used up per hour, with increase of dilution of 0.022 per cent. Thus at the end of the experiment the composition of the dissolving liquid did not differ materially from that at the commencement. It is probable that the above change takes place in two successive stages: first the copper reduces the chromic acid to the sesquioxide, it being itself converted to the oxide; and secondly, these metallic oxides dissolve in the sulphuric acid present. If the movement either of the bullet or of the liquid were insufficient, the temporary formation of a dark green coating on the metal was always observed.

As a preliminary basis it was obviously necessary to prove firstly, that the mass dissolved varied directly with the area, namely, that the values for  $M/A$  under constant conditions of acidity and temperature were constant, and secondly, that under the same conditions two different bullets dissolved at the same rate. In Table I (a) are given (I) the weight in grams of the copper bullet at the commencement of each experiment, (II) its weight at the conclusion, and (III) the difference between (I) and (II) or the quantity dissolved off, (IV) the mean area calculated as explained above, and (V) the value of  $M/A$  expressed as decimilligrams dissolved off per 1 square millimetre per hour. In Table I (b) are given the measurements of the axes in millimetres as a sample of the variations from true sphericity; in other series these measurements will be omitted.

*Mixture Taken.*

59.0 grams potassium bichromate }  
 64.4 ,, sulphuric acid ..... } made up to 1 litre.  
 Temperature 21°.

TABLE I (a).

Weight in grams at commencement.	Weight in grams at conclusion.	Loss.	Mean area in sq. mm.	Value for $\frac{M}{A}$ .
I. 4.7307	4.3585	0.3722	308.75	12.05
II. 4.3585	4.0133	0.3452	293.04	11.89
III. 4.0133	3.6848	0.3285	275.94	11.91
IV. 3.6848	3.3685	0.3163	265.33	11.92
V. 3.3685	3.0658	0.3027	245.61	12.21
VI. 3.0658	2.7838	0.2933	227.63	12.25
Mean value for $M/A$ .....				12.05

TABLE I (*b*).

No.	At commence- ment.	At conclusion.	No.	At commence- ment.	At conclusion.
I., {	10·046 } 10·033 } 10·020 }	9·804 } 9·791 } 9·779 }	IV., {	9·246 } 9·220 } 9·195 }	9·017 } 8·979 } 8·911 }
II., {	9·804 } 9·791 } 9·779 }	9·550 } 9·525 } 9·500 }	V., {	9·017 } 8·979 } 8·941 }	8·738 } 8·708 } 8·674 }
III., {	9·550 } 9·525 } 9·500 }	9·246 } 9·220 } 9·105 }	VI., {	8·738 } 8·708 } 8·674 }	8·376 } 8·319 } 8·280 }

The results given in Table I (*a*) show that under the same conditions the values for the mass dissolved per unit area are constant within an error of +1·5 per cent., and the measurements in Table I (*b*) show that the differences between the greatest and least axes is seldom more than 1 per cent.

In Table II the results are given for another bullet under precisely the same conditions of experiment.

TABLE II.

Weight at com- mencement.	Weight at conclusion.	Loss.	Mean area in mm.	Value for $\frac{M}{A}$ .
4·7649	4·3801	0·3848	309·65	12·43
4·3801	4·0223	0·3578	292·13	12·25
4·0223	3·6795	0·3438	275·71	12·48
3·6795	3·3528	0·3267	258·9	12·60
3·3528	3·0498	0·3030	242·97	12·53
3·0498	2·7773	0·2725	227·09	12·05
Mean value for $M/A$ .....				12·38

The mean value for  $M/A$  obtained with the second bullet is 2·7 per cent. higher than the first bullet under the same conditions, an approximation sufficiently near. The experiments recorded in Tables I and II. are intended only to prove the efficiency of the apparatus and the method of working.

## EFFECTS PRODUCED BY VARIATION OF CONDITIONS.

I. *Temperature.*

To determine the effect produced by variation of temperature a series of experiments were conducted with the following mixture:—

{ 44.2 grams potassium bichromate }  
 { 32.0 „ sulphuric acid ..... } in 1 litre of water.

TABLE III.—*Temperature 21°.*

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value for $\frac{M}{A}$ .
4.6318	4.3858	0.246	306.12	8.04
4.3858	4.1493	0.2365	294.64	8.03
4.1493	3.9208	0.2285	283.8	8.06
3.9208	3.6973	0.2235	272.27	8.23
3.6972	3.4808	0.2165	261.04	8.30
3.4808	3.2006	0.2082	251.38	8.28
Mean value for M/A.....				8.15

TABLE IV.—*Temperature 31°.*

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value for $\frac{M}{A}$ .
4.7160	4.3998	0.3162	309.0	10.23
4.3998	4.0976	0.3022	294.64	10.26
4.0976	3.8041	0.2928	284.94	10.25
3.8041	3.5276	0.2745	266.57	10.30
3.5276	3.2581	0.2695	253.39	10.64
3.2581	3.0156	0.2465	240.45	10.27
3.0156	2.7736	0.2430	228.99	10.61
2.7736	2.5476	0.2270	216.89	10.47
Mean value for M/A.....				10.38

TABLE V.—*Temperature 36°.*

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value of $\frac{M}{A}$ .
4.6647	4.2973	0.3674	304.92	12.05
4.2973	3.9499	0.3474	288.96	12.02
3.9499	3.6199	0.33	273.29	12.07
3.6199	3.3138	0.3061	257.55	11.89
3.3138	3.0253	0.2885	242.29	11.94
2.8200	2.5553	0.2652	216.42	12.25
Mean value for M/A.....				12.04



TABLE VI.—*Temperature 41°.*

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value of $\frac{M}{A}$ .
4.7253	4.3253	0.4002	306.72	13.05
4.3253	3.9523	0.373	290.52	12.84
3.9523	3.5928	0.3595	273.78	13.13
3.2623	2.9558	0.3065	238.82	12.83
2.9558	2.6603	0.2955	222.14	13.31
Mean value of $M/A$ .....				13.03

It will be seen that the difference of the value of  $M/A$  is directly proportional to the differences of the temperatures. This relation will be manifest by the figures given below :—

Temperature.	Value for $M/A$ .	Log $M/A$ .
21°	8.15	0.9114
31	10.38	1.016
36	12.04	1.0805
41	13.03	1.115

Subtracting the first logarithmic value from each of the succeeding, one has—

- (i)  $1.016 - 0.9114 = 0.1047 = 2 \times 0.05335$
- (ii)  $1.0804 - 0.9114 = 0.1692 = 3 \times 0.0564$
- (iii)  $1.115 - 0.9114 = 0.2036 = 4 \times 0.0519$

Thus the differences of the logarithms are practically in the ratio 2 : 3 : 4, which is the same as that of the differences of temperature 10 : 15 : 20. Taking then the mean of the logarithmic differences as 0.0539, and comparing the values given in Tables IV, V, and VI with that of Table III, the observed and calculated results will be as follows :—

Observed values.	Calculated values.
8.15	—
10.38	10.4
12.04	11.84
13.03	13.4

The greatest difference between the observed and calculated values does not exceed 3 per cent., or a variation which might be due to the differences of the rates of solution of individual bullets under identical conditions.

A number of other experiments were made with different mixtures

of potassium bichromate and sulphuric acid to confirm the above relation between temperature and rate of solution.

*Mixture Taken.*

{ 29.0 grams potassium bichromate }  
 { 64.4 „ sulphuric acid . . . . . } in 1 litre water.

TABLE VII.—*Temperature 21°.*

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value of $\frac{M}{A}$ .
4.505	4.2398	0.2652	300.05	8.82
4.2398	3.9863	0.2535	289.53	8.76
3.9863	3.7401	0.2462	276.42	8.87
3.7401	3.5079	0.2322	265.9	8.74
3.2703	3.056	0.2142	242.84	8.82
Mean value of M/A . . . . .				8.80

TABLE VIII.—*Mixture as in Preceding Series. Temperature 31°.*

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value for $\frac{M}{A}$ .
4.7153	4.3755	0.3398	308.5	11.01
4.3755	4.0518	0.3237	292.9	11.05
3.7683	3.4707	0.2976	260.15	11.04
3.4707	3.1848	0.2859	248.85	11.49
3.1848	2.9078	0.277	234.85	11.82
2.9078	2.6488	0.259	220.56	11.75
Mean value for M/A . . . . .				11.36

From the figures given below, it is evident that the difference of the logarithms of the values for M/A is equal to that observed for the difference of 10° in the preceding observations:—

Temperature.	Value for M/A.	Log M/A.	Difference.
21°	8.8	0.9445	0.1108 = 2 × 0.0554
31	11.36	1.0553	

Adopting the above mean value, 0.0539 for 5°, the observed and calculated results will be as follows:—

Observed.	Calculated.
8.8	—
11.36	11.28

*Mixture Taken.*

59.0 grams potassium bichromate } made up with water to 1 litre.  
 32.2 „ sulphuric acid. .... }

TABLE IX.—*Temperature 21°.*

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value for $\frac{M}{A}$ .
4.7419	4.4945	0.2474	312.33	7.92
4.4945	4.2560	0.2385	301.56	7.92
4.256	4.0225	0.2335	290.54	8.04
4.0225	3.8009	0.2216	279.4	7.92
3.8009	3.581	0.2158	266.48	8.10
Value for $\frac{M}{A}$ .....				7.98

TABLE X.—*Mixture as in Preceding Series. Temperature 31°.*

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value for $\frac{M}{A}$ .
4.7278	4.4111	0.3167	308.26	10.27
4.4111	4.1093	0.3018	293.39	10.28
4.1093	3.8185	0.2908	279.64	10.40
3.8185	3.5418	0.2767	266.64	10.39
3.5418	3.2731	0.2687	253.21	10.61
3.2731	3.0228	0.2503	239.86	10.44
Mean value.....				10.4

The difference of the logarithms of the above mean values is given below:—

Temperature.	Value for $\frac{M}{A}$ .	Log $\frac{M}{A}$ .	Difference.
21°	7.98	0.902	
31	10.4	1.0169	0.1159 = $2 \times 0.0574$ .

Observed values.	Calculated.
7.98	—
10.4	10.26

It will be necessary to quote only one more pair of results to illustrate the above relation between temperature and amount dissolved off; these were conducted with the cone apparatus:—

*Mixture Taken.*

{ 44.2 grams potassium bichromate }  
 { 48.0 „ sulphuric acid . . . . . } made up with water to 1 litre.

TABLE XI.—*Temperature 21°.*

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value for $\frac{M}{A}$ .
4.5269	4.2562	0.2704	302.59	8.95
4.2562	3.9942	0.262	289.23	9.06
3.9942	3.7427	0.2515	277.09	9.08
3.7427	3.5087	0.234	265.64	8.81
3.5087	3.2777	0.231	254.02	9.09
3.2777	3.0532	0.2225	242.33	9.19
Mean value . . . . .				9.03

TABLE XII.—*Mixture as in Preceding Series. Temperature 36°.*

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value for $\frac{M}{A}$ .
4.8232	4.4217	0.4015	311.23	12.9
4.2992	3.9229	0.3763	287.53	13.09
3.9219	3.5767	0.3462	271.05	12.77
3.5767	3.2507	0.326	254.51	12.81
3.2507	2.9406	0.31	238.1	13.02
2.9406	2.6542	0.2865	224.79	12.75
2.6542	2.3867	0.2765	207.29	12.9
2.3867	2.1332	0.2525	192.69	13.1
2.1332	1.8969	0.2363	178.65	13.17
1.8969	1.6772	0.2197	166.86	13.17
Mean value . . . . .				13.07

The difference of logarithms will be as follows:—

Temperature.	Value for $M/A$ .	Log $M/A$ .	Difference.
21°	9.03	0.9556	0.1606 = $3 \times 0.0536$ .
36	13.07	1.1162	

Observed values.	Calculated.
9.03	—
13.07	13.11

All the above experiments show that the increment of the rate of solution produced by increase of temperature is independent of the proportions of potassium bichromate and sulphuric acid present, as

also of the degree and kind of motion imparted to the metallic bullet.

The results show that the velocity of chemical action between copper and chromic acid is an exponential function of the temperature, the former increasing in geometrical as the latter increases in arithmetical proportion. This relation may be expressed by the equation—

$$(i) \quad v_t = v_{t_1} e^{k(t-t_1)},$$

$$(ii) \quad v_t = v_{t_1} k^{(t-t_1)},$$

in which  $v_t$  is the velocity at a higher temperature  $t$ ,  $v_{t_1}$  the velocity at a lower temperature  $t_1$ , and  $k$  is a constant. (In equation (i)  $e$  = base of Napierian logarithms.) The value for  $k$  in equation (i) = 0.0108; hence it follows that the velocity is doubled for every increase of 30°.

It is, perhaps, worth calling attention to the very simple relations between temperature and velocity of chemical change, first pointed out by Messrs. Harcourt and Esson in the case of hydrogen peroxide and hydriodic acid (this Journal, 1867, 492). A list of cases investigated which follow the same law is of interest.

Thus the velocity of reaction between potassium chlorate and hydrochloric acid\* is doubled for every 5°, that between hydrogen peroxide and hydriodic acid is doubled for every 10°,† that between ferrous sulphate and potassium chlorate is doubled for every 8° (approximately), that between acetic acid and ethyl alcohol is doubled for every 12°,‡ that between marble and hydrochloric acid is doubled for every 20°,§ and that between copper and chromic acid is doubled for every 30°.

As pointed out by Boguski,|| increase of temperature produces not only an increase of the kinetic energy of the molecules within the liquid but also a decrease of viscosity. Upon these factors, concerning which too little is known at present, depends the numbers of heterogeneous molecules, which have a chance of colliding with one other in any unit interval of time.

## VARIATION OF CONDITIONS.

### II. Sulphuric Acid.

A series of experiments were made in which the only variable in

\* W. H. Pendlebury and Miss M. Seward, *Proc. Roy. Soc.*, **45**, 125.

† J. J. Hood, *Phil. Mag.* [5], **20**, 327.

‡ Berthelot and Pean-St. Gilles, *Ann. Chim. Phys.* [3], **66**, 116. This result is calculated from the data given by the authors; these, though few, are sufficient to show that the chemical change follows the same law. This question has also been discussed by Lemoine, *Études sur les Équilibres chimiques*, p. 178.

§ Spring, *Zeit. physikal. Chem.*, **1**, 219.

|| *Zeit. physikal. Chem.*, **1**, 563.

the conditions was the proportion of sulphuric acid, in order to determine the effect produced by this variation.

*Mixture Taken.*

{ 41.3 grams sulphuric acid. . . . . } made up to 1 litre.  
 { 44.2 „ potassium bichromate. . . } made up to 1 litre.

TABLE XIII.—*Temperature 36°.*

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value for $\frac{M}{A}$ .
4.8033	4.435	0.3683	311.07	11.84
4.435	4.0773	0.3577	294.83	12.14
4.0773	3.7401	0.3372	277.51	12.15
3.7401	3.4282	0.3118	261.92	11.93
3.4282	3.2327	0.2955	247.34	11.95
3.2327	2.9557	0.277	232.41	11.92
2.9557	2.6902	0.2655	217.12	11.94
2.6902	2.4457	0.2445	203.07	12.04
2.4457	2.2157	0.23	190.26	12.07
Mean value . . . . .				12.00

*Mixture Taken.*

{ 35.4 grams sulphuric acid. . . . . } made up to 1 litre.  
 { 44.2 „ potassium bichromate. . . } made up to 1 litre.

TABLE XIV.—*Temperature 36°.*

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value for $\frac{M}{A}$ .
4.7678	4.4438	0.324	308.67	10.50
4.4438	4.1365	0.3073	294.08	10.45
4.1365	3.8403	0.2962	280.15	10.57
3.8403	3.406	0.275	266.53	10.34
3.406	3.154	0.252	240.89	10.46
Mean value . . . . .				10.44

*Mixture Taken.*

{ 29.5 grams sulphuric acid. . . . . } made up to 1 litre.  
 { 44.2 „ potassium bichromate } made up to 1 litre.

TABLE XV.—*Temperature 36°.*

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value for $\frac{M}{A}$ .
4·6438	4·3715	0·2723	303·96	8·96
4·3715	4·1113	0·2601	292·65	9·06
4·1113	3·8601	0·2512	280·82	8·94
3·8501	3·6228	0·2372	268·96	8·82
3·6228	3·3943	0·2205	256·54	8·91
3·3943	3·1681	0·2255	245·5	9·19
Mean value.....				8·98

*Mixture Taken.*

{ 23·5 grams sulphuric acid..... } made up to 1 litre.  
 { 44·2 „ potassium bichromate. }

TABLE XVI.—*Temperature 36°.*

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value for $\frac{M}{A}$ .
4·6632	4·4317	0·2315	310·43	7·46
4·213	3·9927	0·2203	288·65	7·63
3·9927	3·7837	0·209	278·67	7·50
3·7837	3·5877	0·205	268·62	7·63
3·5877	3·3902	0·1965	258·31	7·62
3·3902	3·202	0·1882	247·91	7·58
Mean value .....				7·60

In the above experiments (Tables XII—XVI), the quantities of sulphuric acid, the only variable in the conditions, have been taken in the arithmetical proportion 2 : 1·75 : 1·5 : 1·25 : 1; the values for  $M/A$  are also in an arithmetical proportion (a result *à priori* probable). Thus assuming a common difference of 1·4 between each successive number in the series of the values for  $M/A$ , the values calculated will be—

$$13·2 : 11·8 : 10·4 : 9·0 : 7·6,$$

while those found were

$$13·07 : 12·0 : 10·44 : 8·98 : 7·6.$$

showing a maximum error of 1·5 per cent. between the calculated and the observed numbers.

The increase in the rate of solution is proportional to the quantity of sulphuric acid, or the curve representing the rate of solution as a function of the concentration of the acid is a straight line. The equation for this line is

$$y - 2 = \frac{14}{59} x,$$

in which  $x$  is the number of grams of sulphuric acid per litre, and  $y$  the value for  $M/A$ ; this equation shows that under the same conditions copper would dissolve to a slight extent in an aqueous solution of potassium bichromate of the concentration used in the above experiments, without the presence of the sulphuric acid.

### III. Potassium Bichromate.

A series of experiments were further made to determine the effect produced by variation of the proportion of the potassium bichromate, other conditions being kept constant.

#### Mixture Taken.

{ 21.1 grams potassium bichromate } made up to 1 litre.  
 { 47.2 „ sulphuric acid ..... }

TABLE XVII.—Temperature 36°.

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value of $\frac{M}{A}$ .
4.6813	4.3149	0.2694	314.98	8.53
4.3149	4.057	0.2574	296.81	8.67
4.0575	3.8148	0.2427	285.12	8.51
3.8148	3.5818	0.233	274.17	8.50
3.5818	3.3613	0.2205	263.96	8.34
3.1588	2.9503	0.2055	241.95	8.49
2.9503	2.7533	0.197	232.26	8.48
2.7533	2.5629	0.1904	222.45	8.56
Mean value .....				8.51



*Mixture Taken.*

{ 27·62 grams potassium bichromate } made up to 1 litre.  
 { 47·12 „ sulphuric acid . . . . . }

TABLE XVIII.—*Temperature 36°.*

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value of $\frac{M}{A}$ .
4·6873	4·3475	0·3398	305·6	11·12
4·3475	4·0218	0·3257	290·7	11·21
4·0218	3·7075	0·3133	276·85	11·32
3·7075	3·4173	0·2903	260·34	11·15
3·4173	3·1453	0·272	246·57	11·03
3·1453	2·8668	0·2585	233·15	11·11
2·8668	2·6231	0·2437	218·61	11·15
2·6231	2·3908	0·2323	206·47	11·25
2·3908	2·1226	0·2182	194·03	11·25
Mean value . . . . .				11·17

*Mixture Taken.*

{ 33·15 grams potassium bichromate } made up to 1 litre.  
 { 47·12 „ sulphuric acid . . . . . }

TABLE XIX.—*Temperature 36°.*

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value of $\frac{M}{A}$ .
4·6108	4·2408	0·37	301·53	12·27
4·2408	3·8904	0·3504	286·05	12·23
3·8904	3·3133	0·3396	269·54	12·60
3·3133	3·0248	0·2885	236·56	12·20
3·0248	2·7473	0·2775	220·98	12·56
2·7473	2·4897	0·2576	206·17	12·49
Mean value . . . . .				12·39

*Mixture Taken.*

{ 55.25 grams potassium bichromate }  
 { 47.2     ,,     sulphuric acid     ..... } made up to 1 litre.

TABLE XX.—*Temperature 36°.*

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value of $\frac{M}{A}$ .
4.3905	3.9876	0.4009	290.64	13.73
3.9896	3.6118	0.3778	272.28	13.88
3.6118	3.2651	0.3567	254.61	14.00
3.2651	2.9331	0.332	237.1	14.01
2.9331	2.6418	0.2913	220.8	13.81
2.6418	2.3573	0.2845	206.08	13.81
2.3573	2.0893	0.2680	189.75	14.12
Mean value .....				13.91

*Mixture Taken.*

{ 66.3 grams potassium bichromate }  
 { 47.12     ,,     sulphuric acid     ..... } made up to 1 litre.

TABLE XXI.—*Temperature 36°.*

Weight at commencement.	Weight at conclusion.	Loss.	Mean area.	Value of $\frac{M}{A}$ .
4.656	4.2263	0.4297	306.27	14.03
4.2263	3.8258	0.4005	281.62	14.22
3.8258	3.4238	0.372	262.48	14.17
3.4238	3.0888	0.335	241.08	13.92
3.0888	2.7671	0.3217	226.84	14.21
2.7671	2.4666	0.3002	211.63	14.19
2.4666	2.1875	0.2791	195.13	14.31
Mean value .....				14.15

The results set forth in Tables XVII to XXI and XII are summed up below; the general proportions of potassium bichromate, which were taken in the ratio 1:1.25:1.5:2:2.5:3; in the second column are given the values for  $M/A$ , and in the third are given the difference, either calculated or determined, which correspond to each successive addition of 11.1 grams potassium bichromate.

	Grams.	Grams.	Grams.	Grams.	Grams.	Grams.
Proportion of potassium bichromate .....	22·1	27·62	33·15	44·2	55·2	66·3
Values of $\frac{M}{A}$ .....	8·51	11·17	12·39	13·07	13·91	14·15
Differences .....	5·32	4·36	0·68	0·84	0·24	

It is evident from the above figures that the effect produced by each successive addition of potassium bichromate is at first considerable, then is nearly proportional to the amount of potassium bichromate added, and finally is reduced almost to *nil*. (The numbers 0·67 and 0·84 would become equal if there were an error of less than 1 per cent. in any of the three values 12·39, 13·07, and 13·91.) It is probable that potassium bichromate, when added beyond a certain amount, would merely be so much inert matter, or even so much matter in the way of the colliding molecules of copper and sulphuric acid.

### Conclusion.

The main results embodied in the present paper may be summed up as follows:—

(1.) When a metallic sphere, placed within an acid liquid, receives an equal number of impacts per unit time, or is regularly rotated, it will dissolve uniformly, the amount dissolved off being, as was to be expected, proportional to the surface exposed.

(2.) In the particular case of metallic copper within a solution of potassium bichromate acidulated with sulphuric acid, the amount of metal dissolved off is dependent upon the conditions of (*a*) temperature, (*b*) proportion of sulphuric acid, and (*c*) proportion of potassium bichromate.

(*a*.) If the temperature in degrees be varied in an arithmetical proportion, the amount dissolved off varies in a geometrical proportion. This amount is doubled for every 30°, whatever be the concentration or acidity of the solution. This change is thus perfectly analogous to several others quite different from it and from one another in their nature.

(*b*.) If the quantities of sulphuric acid, other conditions remaining the same, be varied in arithmetical proportion, the amount of metal dissolved off also varies in an arithmetical proportion.

(*c*.) If the quantities of potassium bichromate, other conditions remaining the same, be varied in arithmetical proportion, the amount

dissolved off is at first increased considerably by each successive addition of potassium bichromate, then varies in arithmetical proportion, and finally is but little affected by the amount of potassium bichromate present.

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XLI.—*Experimental Researches on the Periodic Law.* Part I.  
*Tellurium.*

By BOHUSLAV BRAUNER, Ph.D., F.C.S., late Berkeley Fellow of  
Owens College.

*On the Atomic Weight of Tellurium.*

THE atomic weight of tellurium has been determined by Berzelius, who for this purpose oxidised tellurium with nitric acid, and weighed the tellurium dioxide left on ignition. He obtained the following numbers: 128.9 (in 1812), 128.9 (in 1818), and 128.3 (in 1832). In the year 1857, v. Haner, by analysis of the potassium tellurium bromide, found  $\text{Te} = 127.9$ .\* Up to the present time, the round number  $\text{Te} = 128$  has generally been accepted as the true atomic weight of tellurium. (See the atomic weight recalculations by Clarke, Washington, 1882; L. Meyer and Seubert, Leipsic, 1883; and Ostwald, *Lehrbuch*, Leipzig, 1884.)

In the periodic system of elements, however, tellurium lies in Series VI, between antimony = 122 and iodine = 127, and it was therefore assumed by Mendelëeff, that the true atomic weight of tellurium lies between these numbers, and is about 125, as follows:—

Sb.	Te.	I.
122	125	127

According to the recent determinations made by J. P. Cooke, as well as those of Stas, these elements have the following atomic weights,  $\text{Sb} = 119.96$  and  $\text{I} = 126.86$ , and we may therefore expect that the atomic weight of tellurium will be still smaller than the above, namely, about 123.5.

\* All atomic weights used in this paper refer to the standard  $\text{O} = 16$ , for reasons published by me in the *Chemical News*, 58, 307, and *Ber.*, 22, 1186, of May 27th, 1889. My arguments were, I may say, accepted as valid by Horstmann (*Bert. Ber.*, 22, R. 85) and Ostwald (*ibid.*, 1021), although not by Lothar Meyer and Seubert (*ibid.*, 22, 872—879). The numbers used are  $\text{O} = 16$ ,  $\text{S} = 32.07$ ,  $\text{Cu} = 63.3$ ,  $\text{Br} = 79.963$ ,  $\text{Ag} = 107.938$ .

This circumstance caused Wills (*Chem. Soc. Journ., Trans.*, 1879, 704—713) in 1879 to redetermine the atomic weight of tellurium. By the oxidation of tellurium with nitric acid (I), Wills obtained numbers varying between  $\text{Te} = 126.63$  and  $129.66$ . Oxidation with aqua regia (II), gave  $\text{Te} = 128.09$  and  $128.30$ . Lastly, analysis of potassium tellurium bromide gave  $\text{Te} = 126.39$ — $127.93$ . Wills concludes from his experiments “that the atomic weight of tellurium *does not lie* between those of iodine and antimony, but is greater than the former element, which must, therefore, precede tellurium in Mendeléeff’s classification.”

I may be allowed to remark that the differences between the maxima and minima of the numbers obtained by Wills as the atomic weight of tellurium differ in the Series I (see above) by 3.03 units, in Series II by 0.21, and in Series III by 1.57 units, those of the three series showing a distance of 3.27 units and, as 21.4 per cent. of Wills’ numbers are *lower* than the atomic weight of iodine, it is certainly strange to see that from such discordant results a conclusion of such great theoretical importance should be drawn.

It has been shown lately by Basaroff (*J. Russ. Chem. Soc.*, 1887, 61—73), that in the same manner as the elements follow each other in the periodic system, their atomic weights are found to increase, so that the regular variation of quotients obtained by dividing the atomic weight of an element by that of the next lower one may be represented graphically in a satisfactory manner, and it was therefore still more probable that the said regularity should hold good also in the case of tellurium, and that a lower value would be obtained for its atomic weight than that of iodine,  $\text{I} = 126.86$ .

The object of the following research was to undertake a thorough revision of the atomic weight of tellurium, and to that research I have devoted the greater part of my spare time during the past six years.

It was to be expected that tellurium would not remain an exception to the periodic law, for although nearly one-third of the known elements would not have fitted into the periodic system with their originally accepted atomic weights, yet hitherto it has been found that these atomic weights are at fault, and not the system. These apparent exceptions are: Li, Be, Sc, Ti, V, Co, Ga, Y, Nb, Mo, Ru, In, Sb, Cs, La, Ce, Ta, Os, Ir, Pt, Bi, Au, Th, and U.

#### *Preparation of Material.*

Two kinds of material were used for the preparation of pure tellurium: Hungarian tellurium ores, nagyagite, sylvanite, and petzite and Hungarian crude tellurium. After bringing the tellurium into solution in the form of chloride, it was precipitated in the usual

way with sulphur dioxide in the elementary state, and this precipitate, after drying, was fused with potassium cyanide in order to get rid of any selenium which might be present, although none could be detected in it,\* and also of traces of the heavy metals which are carried down with the tellurium on precipitating it with sulphur dioxide. From the claret-coloured solution of potassium telluride, tellurium was precipitated by means of a current of air. Lastly, it was placed in little porcelain boats which were introduced into a wide Bohemian glass tube, surrounded by wire gauze, and then distilled in a current of hydrogen. Minute traces of tellurides of the heavy metals were left behind.

The distilled tellurium forms a crystalline mass of silvery lustre which does not change its colour on exposure to the air. During distillation, part of the tellurium combines with hydrogen, forming tellurium hydride which, before escaping from the heated tube, is again decomposed with deposition of beautiful needle-shaped crystals of the element measuring 1 cm. or more in length; the hydrogen formed, however, always contains some gas of an extremely disagreeable odour which behaves like tellurium hydride, and has very poisonous properties.

By this costly process, large quantities of tellurium were prepared, the properties of which are those required of pure tellurium, according to the present state of our knowledge; it may be redistilled in hydrogen without leaving any residue, and no impurities can be detected in it by qualitative analysis.

#### *Determination of the Atomic Weight.*

It was my intention to determine the atomic weight of tellurium by as many independent methods as possible, but in the course of this investigation it was found to be very difficult to devise methods which would answer the purpose. In this, as in many other respects, tellurium approaches its next horizontal "atomanalogue," antimony, of which Berzelius said in 1812: "I have never worked with a material with which it was so extremely difficult to obtain constant results." (*Schweiger*, 6, 149.)

All the reagents used in the course of the present investigation, as hydrochloric, nitric, and sulphuric acids, were subjected to fractional distillation from platinum vessels, and the water employed was redistilled with alkaline permanganate, and the steam cooled in a platinum condenser; the set of weights used was corrected by the method of vibrations.

\* Having been probably volatilised by the repeated evaporations with strong hydrochloric acid employed to get rid of nitric acid.

*A. Conversion of Tellurium into the Dioxide.*

Tellurium was oxidised (*a*) with nitric acid ; (*b*) with aqua regia.

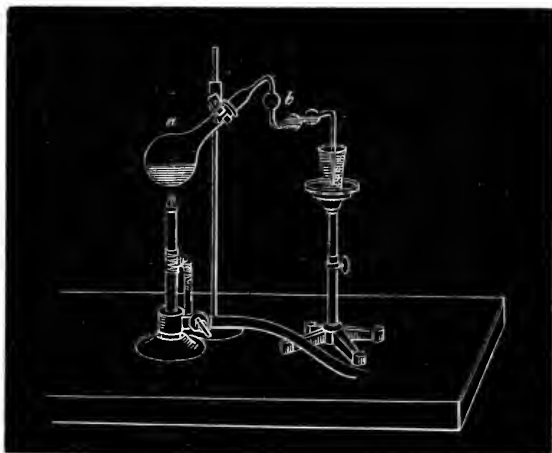
(*a.*) *Oxidation with Nitric Acid.*—The finely powdered tellurium was treated in Experiments 1 and 2 in a platinum crucible with dilute nitric acid, in which it readily dissolves. The crucible was covered with a watch-glass, in order to avoid loss by spirting. After the reaction was over, the contents of the crucible were evaporated to dryness on a water-bath, and then heated slowly up to 400°. It was observed, however, that the basic tellurium nitrate formed loses its last trace of nitric acid at a temperature at which part of the tellurous anhydride contained in the crucible begins to volatilise, the watch-glass becoming covered with a white substance.

Experiment No. 3 was carried on in a flask of hard Bohemian glass (previously boiled with aqua regia) so that the volatile portions were condensed in its colder neck. This method was abandoned, as it did not give constant results.

Exp. No.	Tellurium. grams.	Te dioxide. grams.	Atomic weight.
1. ....	1.9509	2.4437	126.7
2. ....	0.9212	1.1523	127.6
3. ....	1.2947	1.6267	124.8

(*b.*) *Oxidation with Aqua Regia.*—Weighed quantities of pure powdered tellurium were placed in a round-bottomed flask of hard Bohemian glass, Fig. 1 (previously boiled for many days with aqua regia), and, after introducing some hydrochloric acid, nitric acid was

FIG. 1.

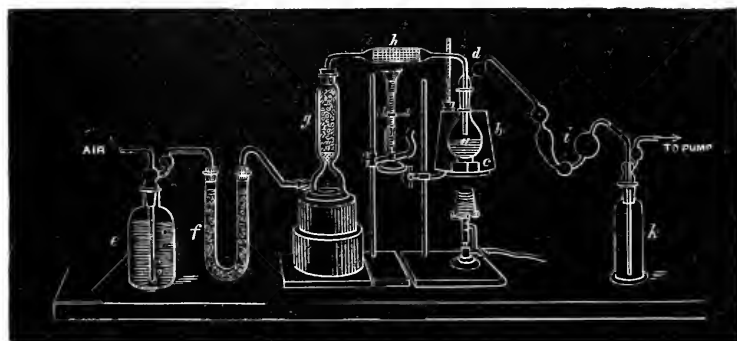


added gradually. As, however, large quantities of the finely divided spray of the solution are carried over with the escaping gases, the neck of the flask was closed with a glass tube, *b*, containing bulbs in the middle, the wider end of which was tightly ground into the neck of the flask, the narrow end dipping into a small beaker containing nitric acid. The escaping gases are thus forced to pass through the nitric acid contained in the small bulbs and in the beaker, and in this way the escaping spray of tellurium solution is completely condensed.

The arrangement of this simple apparatus is seen from Fig. 1, and it was used several times during the course of the present investigation when weighed quantities of substance had to be dissolved without any of the latter being carried off with the escaping gases.

On evaporating the solution of tellurium in aqua regia, some of the tellurium tetrachloride formed is volatilised—a circumstance which was overlooked by Wills—and, further, during the evaporation, organic substances contained in the air may be condensed in it, causing a subsequent reduction at a higher temperature. In order to avoid these sources of error, the solution of tellurium was evaporated in a current of pure, dry air in an apparatus the arrangement of which is seen from Fig. 2. Air from the open was aspirated through potash solution, *e*, a long layer of cotton-wool, *f*, over pumice-stone soaked

FIG. 2.



with sulphuric acid, *g*, and then passed through a tube, *h*, containing red hot platinum sponge. This tube ended in *d*, which is ground into the flask *a* containing the tellurium solution, and heated in an air-bath, *b*, the bottom of which was protected from the direct action of the radiant heat by a screen, *c*, made of asbestos cardboard. The glass bulbs *i* and flask *k* serve for the condensation of the acids escaping from the flask *a*. The various single pieces of which this apparatus



is composed are connected either by air-tight ground glass joints or by fusing them together, without the use of cork or rubber anywhere.

The distilled mixture of hydrochloric and nitric acids, on evaporation with sulphuric acid, gives several milligrams of basic tellurium sulphate (see below, B), but it is a question whether the whole of the escaping tellurium can be collected in this way. However, on neglecting even this small quantity of tellurium, the atomic weight will be found to be higher by 1.2 units. After evaporation to dryness, the residue in the flask was repeatedly evaporated down with nitric acid in a current of air at  $110^{\circ}$ , and finally heated to  $440^{\circ}$ . It was found, however, that at the point at which tellurium trioxide decomposes into the dioxide and oxygen the dioxide begins to volatilise; moreover, when the "tellurium dioxide" after weighing was treated with hydrochloric acid, a white residue was always left, and this would not dissolve in the acid even on continued boiling!

Exp. No.	Te. grams.	TeO <sub>3</sub> . grams.	Atomic weight.
4. ....	2.3092	2.9001	125.0
5. ....	2.8153	3.5332	125.5
6. ....	4.0176	5.0347	126.4
7. ....	3.1613	3.9685	125.3
8. ....	0.8399	1.0526	126.4

#### B. *Conversion of Tellurium Dioxide into the Basic Sulphate.*

As Marignac (*Archives Sc. Phys. Nat.* [3], **10**, 17, separate copy) had succeeded in determining the atomic weight of bismuth by the conversion of the oxide into the sulphate, a similar method was tried with tellurium dioxide. For this purpose, tellurium dioxide was dissolved in hydrochloric acid, and the solution (containing always some undissolved white substance) was evaporated to dryness with a slight excess of sulphuric acid. As soon as the hydrochloric acid had been driven off, beautiful, glistening crystals—rhombic scales—of basic tellurium sulphate,  $\text{Te}_2\text{O}_4\text{SO}_3$ , were left. Sometimes beautiful, regular crystals—combinations of the cube with octohedron—were observed, but these seem to be another salt. It was remarkable that when this operation was carried on in platinum crucibles lower results were obtained (Experiments 9, 10, 11), whereas in glass or porcelain vessels (Experiments 12 and 13) the excess of sulphuric acid could not be driven off without the sulphate undergoing partial decomposition, so that the results obtained were very high.

Exp. No.	TcO <sub>2</sub> . grams.	Tc <sub>2</sub> SO <sub>7</sub> . grams.	Atomic weight.
9. ....	2.4437	3.0570	127.5
10. ....	1.0526	1.3202	125.5
11. ....	1.1523	1.4461	125.0
12. ....	5.0239	6.2182	136.4
13. ....	2.9818	3.7197	129.4

*C. Conversion of Tellurium into the Basic Sulphate.*

Tellurium was first converted into the dioxide, and the latter into the sulphate. Experiments 14—19 were made in platinum crucibles, and they give again lower results than Experiment 20 which was made in a glass flask.

Exp. No.	Tc. grams.	Tc <sub>2</sub> SO <sub>7</sub> . grams.	Atomic weight.
14. ....	1.9509	3.0570	127.1
15. ....	0.9212	1.4461	126.4
16. ....	0.8399	1.3202	125.9
17. ....	0.5836	0.9166	126.2
18. ....	0.5243	0.8261	125.1
19. ....	1.5464	2.4405	124.6
20. ....	5.1674	8.0271	130.0

The method was given up as, in spite of the greatest care, it was found to be impossible to obtain constant results.

*D. Synthesis of Silver Telluride.*

Chemically pure silver (preparation see below) was weighed in a porcelain boat, and tellurium vapour passed over it while it was heated in a porcelain tube in a current of carbon dioxide. The latter was purified by passing it over hot sodium carbonate, and then over red hot silver and copper wire. On allowing it to cool in a current of the same gas, silver telluride having approximately the composition Ag<sub>2</sub>Te remained in the boat as a fused, crystalline mass of metallic lustre.

*Experiment 21.*—1.1434 grams of silver gave 1.8019 grams of silver telluride (containing 0.6585 Te). From this the atomic weight Te = 124.3 is calculated. It may be that the interior of the mass contains uncombined metallic silver which escaped the action of the tellurium vapour, and therefore a fresh portion of finely divided silver was mixed with an excess of powdered tellurium, and this mixture was first fused in a current of carbon dioxide, and then strongly heated.

It was found that the silver telluride obtained was more brittle and

more easily fusible than that just described, and that it contained an excess of tellurium over that required by the formula  $\text{Ag}_2\text{Te}$ ; whereas, when its composition approaches that formula, it does not melt even at a strong red heat, and is far less brittle.

*Experiment 22.*—From 0.5382 gram of silver, the following quantities of telluride were obtained:—

	Time of heating in hours.	Telluride, grams.	Atomic weight.
(a.)	4	0.8607	129.5
(b.)	7	0.8589	128.6
(c.)	15	0.8560	127.5

In order to drive off any excess of tellurium which might have remained in the interior of the fused mass, the telluride was powdered and heated again for five hours. It did not fuse again, and its weight was finally 0.8513 gram. This corresponds with  $\text{Te} = 125.6$ .

*Experiment 23.*—1.0796 grams of silver was mixed with an excess of tellurium and heated in the way described. After three hours, 1.8906 grams of silver telluride was formed; after 11 hours, 1.7194 grams. Hydrogen does not reduce this compound to pure silver, on the contrary, silver seems to combine more readily in its presence with an excess of tellurium, and the latter is given off with greater difficulty. The result was 1.7187 grams, calculation from which gives  $\text{Te} = 127.8$ .

*Experiment 24.*—In order to obtain a very high temperature, a Fletcher tube-furnace, acting with or without blast, was used. The boat containing the tellurium and silver was heated for half an hour to redness, and then, for 10 minutes only, to a yellow heat, as otherwise the boat fuses to the inside of the porcelain tube. 0.4917 gram of silver yielded 0.7835 gram of telluride, from which  $\text{Te} = 128.1$ .

It is seen from these experiments that at a point at which the silver telluride contains for 2 atoms of silver 127.5 to 128.1 parts of tellurium, the excess of the latter is driven off with the greatest difficulty. If, however, the surface of the telluride is artificially increased, dissociation of the silver telluride begins to take place.

The partial synthesis of silver telluride does not give results sufficiently exact for the determination of the atomic weight of tellurium.

### E. *Synthesis of Copper Telluride.*

Copper combines with tellurium with far greater energy than silver does, so that a telluride of the composition  $\text{Cu}_2\text{Te}$  absorbs further quantities of tellurium if heated in its vapour, this absorption again

going on better in an atmosphere of hydrogen than in one of carbon dioxide.

The copper employed in these experiments was prepared by Hampe's method (*Zeit. anal. Chem.*, 1874, 352), that is, electrolysis of a copper solution from which the impurities had been removed by partially precipitating with potassium hydroxide. Before experiment, the pure copper was heated in a current of hydrogen and allowed to cool in an atmosphere of carbon dioxide.

As the polytellurides of copper formed at first (they are interesting compounds and alloys) give off the excess of tellurium above that required by the formula  $\text{Cu}_2\text{Te}$  with far greater difficulty than the silver polytellurides, the full heat of the Fletcher blast tube-furnace had to be employed. The mixture of copper and tellurium was contained in a small porcelain boat, the outer glaze of which had been removed by etching with hydrofluoric acid. This boat was placed in a larger one, filled up to the edge with Calais sand, and this second boat was placed on a layer of sand in the porcelain tube in order to avoid the chance of the different porcelain vessels fusing together. The synthesis of the copper telluride was effected in the same manner as that of the silver telluride, the temperature being of course considerably higher.

Of the numerous experiments made, only a typical one need be mentioned here.

*Experiment 25.*—The copper telluride was weighed after being heated for a definite length of time to a yellow heat, and then heated again. It will be seen that the quantity of tellurium given off is smaller the more nearly we approach a telluride of the composition  $\text{Cu}_2\text{Te}$ .

From 0.5033 gram of copper, the quantities of telluride given in the second column were obtained:—

	Time of heating.	Copper telluride.	Loss of Te per minute.	Atomic weight.
(a.)	5 min.	1.1316	—	—
(b.)	15 „	1.0533	0.0078	—
(c.)	25 „	1.0207	0.0033	130.2
(d.)	30 „	1.0108	0.0020	127.7
(e.)	35 „	1.0044	0.0013	126.1

The copper telluride, prepared by fusion in a current of carbon dioxide, is a steel-blue, crystalline mass, the surface of which was in Experiment 25(e) covered with small blisters, which seems to prove that the compound  $\text{Cu}_2\text{Te}$  contains a small quantity of free copper.

On continued heating of the copper polytellurides to redness in a

current of hydrogen, beautiful rhombohedra of a telluride possessing a steel colour and great lustre were obtained.

### F. *Synthesis of Gold Telluride.*

Polytellurides of gold (alloys of gold and tellurium) are crystalline compounds of a silvery lustre. Heated to redness in a current of carbon dioxide, they easily dissociate, leaving finally a mixture of white gold telluride,  $\text{Au}_2\text{Te}$ , with yellow gold. I shall not give here any account of the individual experiments, as they cannot be used for the determination of the atomic weight of tellurium.

All these briefly mentioned metallic tellurides obtained by synthesis are interesting instances partly of definite compounds, partly of alloys. They confirm the law enounced by Beketoff ["Researches on the Phenomena of Displacement," Charkoff, 1865 (in Russian)] in 1859 and 1865, that the affinity of two heterogeneous bodies to each other is the greatest when the weights of the masses taking part in the reaction are equal. This is seen from the following group:—

$$\text{Cu}_2 : \text{Te} = 126 : 126$$

$$\text{Ag}_3 : \text{Te} = 216 : 126$$

$$\text{Au}_2 : \text{Te} = 394 : 126$$

and at the same time it may be remarked that the stability at a high temperature considerably decreases from the highest member ( $\text{Cu}_2\text{Te}$ ) to the lowest ( $\text{Au}_2\text{Te}$ ).

### G. *Analysis of Tellurium Dioxide.*

Pettersson and Ekman have determined the atomic weight of selenium by the reduction of selenium dioxide with sulphurous acid and weighing the selenium precipitated. The same method was used by me for the determination of the atomic weight of tellurium.

Pure tellurium dioxide was prepared by dissolving distilled tellurium in aqua regia, evaporating the solution several times with distilled nitric acid, and fusing the residue in small portions in a platinum crucible. After a short fusion, the tellurium dioxide is obtained in the form of a brittle, crystalline mass of a milk-white or cream colour, which becomes yellow or brownish-yellow as soon as the fusion is continued more than is absolutely necessary.

Weighed quantities of the powdered dioxide were dissolved in hydrochloric acid in the glass apparatus, Fig. 1 (p. 385), in order to avoid loss by the volatilisation of the tetrachloride formed. The yellow solution obtained was mixed in the same flask with concentrated sulphurous acid, and it was remarked that the tellurium precipitated is some-

times so finely divided that it forms a transparent solution of a dark greenish-blue, blue, or violet colour.\* The solution was heated to 60—70° and completely saturated with sulphur dioxide; this caused a separation of tellurium in a flocculent state. After heating the solution for some time in order to produce complete reduction and separation, the precipitate was washed first with dilute sulphurous acid and then with water, but the finely separated tellurium is so easily oxidised that a small portion always goes into solution, so that the filtrate, after concentration and treatment with sulphurous acid, always gives small quantities of tellurium. This tendency of finely divided tellurium to oxidation is so great, that after standing for some time with cold hydrochloric acid in contact with air, considerable quantities pass into solution as tellurium tetrachloride, whereas tellurium alone is insoluble in cold hydrochloric acid.

The oxidation of tellurium is more apparent when it is dried at 100°, as is seen from the following:—

*Experiment 26.*—3·8745 grams of tellurium dioxide were reduced in the manner described, and dried on a weighed filter at 110°. Theory (see H) requires 79·93 per cent. Te. The quantity of tellurium obtained weighed—

(a.)	After 2 hours . . . . .	3·1249 grams = 80·63 p. c.
(b.)	After further 6 hours	3·1279 „ = 80·71 „
(c.)	„ „	3·1396 „ = 81·01 „

This large increase in weight is partly due to the cause mentioned below.

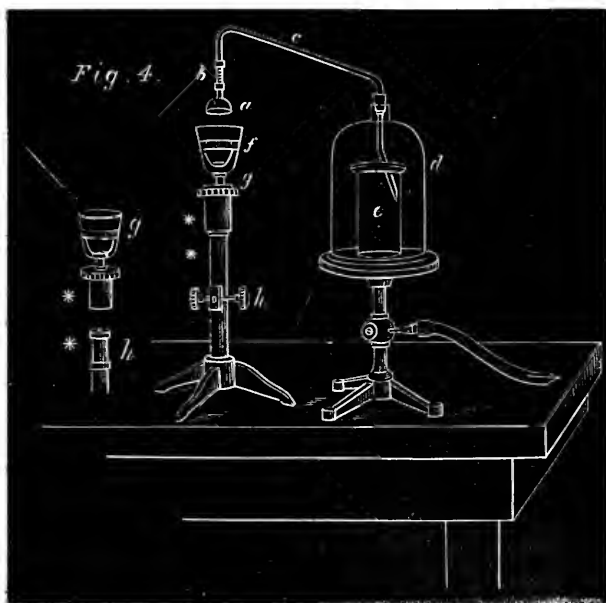
The results obtained on drying the precipitated tellurium in a vacuum or in a current of carbon dioxide are not much better, as after fusion of such tellurium in a current of pure hydrogen, drops of water are obtained, proving that the tellurium has been partly oxidised during washing.

Finely divided tellurium passes through glass-wool, asbestos, or even artificial pumice-stone, so that, in order to avoid the use of weighed paper filters, the method of reversed filtration was used for its collection with a slight modification, which will be understood from the accompanying drawings, Figs. 3 and 4. The upper part of the stand† carrying the crucible can be taken off, and is so arranged that the crucible carrying the liquid to be filtered cannot be easily upset, a circumstance of great importance when, for example, the

\* Selenium gives, under similar circumstances, solutions of a beautiful intense blue colour.

† This stand was made of excellent workmanship by Messrs. Jos. and Jan Frie, mechanics, Prague.

filtration of silver bromide is effected in a nearly dark room. The tellurium was washed finally with alcohol and dried at  $110^{\circ}$  in an atmosphere of hydrogen.



Unfortunately it was found here that considerable quantities of sulphuric and hydrochloric acid are carried down with the tellurium from the solution in which it is precipitated, but these could be removed to a very great extent by heating it, after taking out the filter, in a current of hydrogen to about  $300^{\circ}$ . The results are then pretty nearly accurate, as seen from—

*Experiment 27.*—2.5489 grams of tellurium dioxide, after reduction with sulphurous acid and drying at  $130^{\circ}$  in a current of hydrogen in the same flask which served for its precipitation, gave (a) 2.0389 grams of tellurium. From the filtrate (b), 0.0047 gram was obtained.

The portion (*a*) was heated in a current of hydrogen at 300° in a flask similar to that represented by *a, d* in Fig. 2 (p. 386), and it was found that the escaping vapours gave with silver nitrate solution a white, and not a black, precipitate, a proof that only hydrochloric acid and no tellurium hydride was formed. The loss of weight was equal to 0.0062 gram, so that the real weight of the tellurium was 2.0374 grams.

From this, the atomic weight of tellurium is calculated as  $\text{Te} = 127.5$ , and the percentage composition of the dioxide as

Tellurium . . . .	79.93
Oxygen . . . . .	20.07
	<hr/>
	100.00

#### H. Analysis of Tellurium Tetrabromide.

The methods described under *Aa, Ab, C, D, E*, and *F*, gave for the atomic weight of tellurium numbers varying but little from the theoretically expected number,  $\text{Te} = 125$ , and from these results it would have been correct to assume that number as the true atomic weight of tellurium—as the author actually did for some time—especially had there been a better agreement between these numbers, a circumstance which, as shown above, was unfortunately never met with in the case of tellurium.

Of all the methods hitherto mentioned in this paper, that described under *F* alone seems to yield favourable results, although with some difficulty; here, however, we have the most unfavourable case of an atomic weight determination, viz., weighing the tellurium, resulting from an analysis, in the elemental state.

I expected to obtain good results from the analysis of tellurium tetrabromide, as the gravimetric, and especially the volumetric estimation of combined bromine are, according to Stas (see especially his latest classical research, *Mémoires de l'Académie Royale de Belgique*, **43** [2], 1—105), the most exact of all quantitative determinations. This method has been applied lately with great success to the determination of the atomic weight of antimony by J. P. Cooke (*Proc. Amer. Acad.*, **13**, 1—71; **15**, 251—255; and **17**, 13—22), in the case of aluminium by Mallet (*Phil. Trans.*, 1880; *Chem. News*, **45** and **46**), for titanium by Thorpe (this Journal, *Trans.*, 1885, 108), and in the case of gold by Thorpe and Laurie (*Trans.*, 1887, 565).

Neither the gravimetric nor the volumetric determination of chlorine in chlorides answers the same purpose on account of the comparatively great solubility of silver chloride in water, and in the solutions employed, as is shown in a most remarkable research pub-



lished by Stas ("Recherches de Statique Chimique," *Ann. Chim. Phys.* [4], **25**, 22--94; [5], **3**, 145--188 and 289--327).

*Preparation of Pure Bromine.*

The pure bromine employed was prepared by two methods, the first being that recommended by Stas. For this purpose commercial bromine was first repeatedly shaken with water, dissolved in a concentrated solution of calcium bromide (prepared from the same bromine, calcium hydroxide, and ammonia), precipitated with water, and dried over calcium bromide and oxide. The last trace of water was removed with phosphorus pentoxide, which had been resublimed in a current of dry air.

The second method consisted in distilling potassium bromide (350 grams) dissolved in water (500 grams) with a quantity of chromic mixture (150 grams of potassium dichromate dissolved in 600 grams of pure sulphuric acid and mixed with 500 grams water) insufficient for its complete decomposition. In order to avoid dangerous explosions resulting from the heat developed by the reaction, the large retort containing the mixture was immersed in a large vessel of water at about 65°. The quantity of crude bromine obtained in this way from the above mixture weighed 210 grams instead of the theoretical amount of 235.1 grams.

In order to purify this bromine from the last traces of iodine and chlorine, a process recommended by Stas (*Mém. Ac. Belye*, **43**, 90--93), but not sufficiently known to chemists, was used. This consists in distilling 400 grams of bromine from a mixture of 300 grams of water, 250 grams of potassium bromide and 25 grams of granulated zinc oxide (prepared by heating pure basic zinc nitrate to a white heat). The same mixture may be used for the rectification of two successive portions of bromine of 400 grams each. The bromine obtained was dried over anhydrous calcium bromide and oxide, and the last trace of water was removed by means of anhydrous barium oxide.

The bromine prepared by either of these methods was distilled in an apparatus consisting entirely of glass. It was found to boil at 63°, but on treating a portion of it with potassium hydroxide the smell of an organic bromine compound could be perceived, probably bromoform or carbon tetrabromide, due to the action of bromine on particles of dust and filter-paper, unavoidably present in the reagents used (cf. Hamilton, *Trans.*, 1881, 48). We must regard with admiration the great care taken by Stas, when he prepared bromine which was quite free from any carbon compound containing bromine.

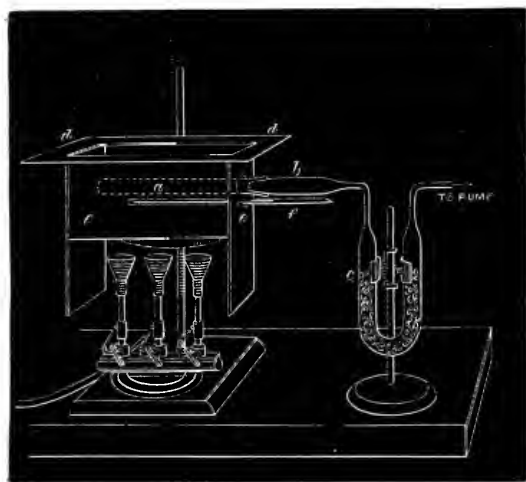
*Preparation of Tellurium Tetrabromide.*

In order to prepare the tetrabromide, a combustion-tube of the best Bohemian glass was used, which was sealed and rounded at one end and was widened conically at the open end; into the latter were carefully ground (a) the tube of a Drechsel gas wash-bottle, and (b) a glass tube of a similar diameter, drawn out a little at the other end and sealed to a U-tube.

The sublimation-tube was placed vertically in cold water, several grams of pure bromine poured into it, and then very finely powdered tellurium was gradually added in small portions, shaking the liquid contents from time to time. In order to remove the excess of bromine, the Drechsel "Aufsatz" was inserted into the open end and the tube was heated in warm water while a current of dry carbon dioxide was passed through; the tellurium tetrabromide was then left in the tube as a beautifully yellow, loose mass. The product, however, is not pure, as it contains in its interior some free tellurium which has escaped the action of the bromine. On heating this mixture to a higher temperature, tellurium dibromide is formed thus:  $\text{TeBr}_4 + \text{Te} = 2\text{TeBr}_2$ . The tetrabromide cannot be fused or boiled at the ordinary pressure without undergoing partial decomposition into free bromine and the greenish-black dibromide,  $\text{TeBr}_4 = \text{TeBr}_2 + \text{Br}_2$ . The lower compound gives a deep-violet vapour.

After numerous experiments, the following method was used for the preparation of pure tellurium tetrabromide for analysis. The glass tube a, Fig. 5, containing the yellow tetrabromide, was connected

FIG. 5.



with the tightly ground tube, *b*, which, by means of a drying tube, *c*, filled with pumice moistened with sulphuric acid, was connected with a pump. The greater portion of the lower part of the sublimation-tube *a* was heated in an air-bath, *ee*, made of pieces of asbestos cardboard joined by means of platinum wire. The bath could be covered with a mica plate, *dd*, in order to watch the behaviour of the bromide with rise of temperature, and in the same level as the sublimation-tube a thermometer, *f*, was placed horizontally. A vacuum was then made in the tube, and its temperature raised to 200°. At this temperature, the more volatile dibromide could be separated by *fractional* sublimation from the less volatile tetrabromide, which remained behind in the lower part of the tube, and it was found possible to drive the subliming dibromide quite out of the tube *a* into the tube *b*. On now raising the temperature of the air-bath to about 300°, the tetrabromide is found to sublime without leaving any residue, and to condense on the colder walls of the tube in the form of beautiful, fiery-red, crystalline crusts which become orange-coloured on cooling. If there had been any oxybromide present, it would have decomposed, leaving a residue of tellurium dioxide, thus:  $2\text{TeOBr}_2 = \text{TeBr}_4 + \text{TeO}_2$ , as shown by special experiments with a bromide prepared from superficially oxidised tellurium.

The crusts of pure tetrabromide are very brittle, easily detached from the walls of the tube, and not hygroscopic when weighed in a small weighing bottle made of thin glass, closed with a well-ground stopper; an empty bottle of equal size was always placed on the other pan of the balance. By the method of vibrations, the weight of the substance could be determined within a few hundredths of a milligram.

The bromide dissolves easily in a solution of tartaric acid (2 parts) in water (2 parts) without leaving any appreciable residue, but on using a more dilute solution, decomposition takes place accompanied by the separation of sparingly soluble telluric acid. The orange-coloured solution contains tellurium tetrabromide, but on addition of water its colour disappears and it then contains a hydrobromic acid solution of tellurium tartrate. Had the bromide contained any trace of oxybromide, telluric acid would have been left undissolved.

In a preliminary experiment, a tartaric acid solution of tellurium tetrabromide was precipitated by silver nitrate in the ordinary way and the silver bromide weighed.

*Experiment 28.*—3.1591 grams of tellurium tetrabromide yielded 5.3612 grams of silver bromide. From this  $\text{Br} = 72.22$  per cent. This would correspond to an atomic weight of  $\text{Te} = 123.0$ . Subsequent exact experiments, however, have shown that the percentage of bromine is in reality only  $= 71.48$ , so that the silver bromide must have been too heavy by 0.0552 gram.

A detailed examination into this source of error has shown that it is due to two circumstances.

Firstly, it was found that in concentrated solutions containing tellurium, tartaric acid, and bromine, silver nitrate gives a precipitate consisting of silver bromide, which settles rapidly, and also of glistening, crystalline scales, which separate slowly from the liquid and are deposited on the surface of the first precipitate. They consist of tellurium silver tartar emetic, and have probably the composition  $(C_4H_4O_6)_2Ag_2(TeO), 2H_2O$ , as shown by the following analysis:—

*Experiment 29.*—0.4660 gram gave 0.1913 gram silver chloride.

Calculated.	Found.
31.2	30.9

The analogous citrate seems to have a more complicated formula.  $(C_6H_5O_7)_2Ag_3H(TeO), 2H_2O$ .

*Experiment 30.*—0.6491 gram gave 0.3205 gram silver chloride.

Calculated.	Found.
36.7	37.1

The tartrate exhibits the most complete analogy to antimony, for Cooke has observed that in a tartaric solution of antimony tribromide, silver nitrate causes the formation of  $(C_4H_4O_6)Ag(SbO), H_2O$ .

In order to avoid the formation of silver tellurium tartar emetic and its precipitation along with the silver bromide, the precipitation of silver bromide was effected in the presence of a sufficient quantity of water and of nitric acid, in which this substance is easily soluble; and all excess of silver nitrate was avoided, as the substance is formed only when an excess of silver nitrate over that required to form silver bromide is present.

The second cause of the higher weight of the silver bromide precipitated in Experiment 32 is the circumstance that silver bromide readily carries down with it foreign substances contained in the solutions from which it is precipitated; it acts in this way with tellurium tartrate, as is seen from its becoming black in contact with zinc and water. This can be avoided only when, following Stas' directions, the silver bromide is vigorously shaken with the solution from which it has been precipitated, and with the water containing a little nitric acid used for washing it—of course in perfect darkness. Indeed, it is found that in this way a pure silver bromide, containing no tellurium, is obtained.

Several preliminary experiments carried out in this way, gave results approaching the truth, but they are omitted in order to avoid everything superfluous, although the first experiments seemed to point to insurmountable difficulties.

*Experiment 31.*—3·82048 grams of tellurium tetrabromide, after being dissolved in tartaric acid, were precipitated with the requisite amount of silver nitrate, washed by repeatedly shaking, and the silver bromide was collected by the method of reversed filtration. Its weight was 6·41734 grams = 71·482 per cent. of bromine. From this, the atomic weight of tellurium is calculated as  $\text{Te} = 127·61$ .

After this, the combined gravimetric and volumetric method was used for the analysis of tellurium tetrabromide.

### *On Pure Silver and its Properties.*

Pure silver was prepared by two methods given by Stas.

*A.* Purest silver from the Mint was dissolved in distilled nitric acid, and the solution of the fused nitrate precipitated with distilled hydrochloric acid. After washing the chloride by prolonged agitation, it was boiled with aqua regia, and reduced with pure milk-sugar and sodium hydrate. The metal was boiled out with dilute sulphuric acid, digested with ammonia, and fused under borax and nitre in a Paris crucible. After pouring it into moulds of kaolin, the bars were rolled out into thin ribbons, between hard steel rollers well oiled, and the thin plates cleaned with sea-sand, ammonia, and alcohol. After cutting into pieces of about a gram and its subdivisions, they were treated with hydrochloric acid and ammonia, and finally heated in a porcelain crucible nearly to the melting point of silver.

*B.* Ordinary alloy of silver and copper from the Mint containing 0·900 of the former metal, was dissolved in nitric acid, and the mixed nitrates of silver and copper fused for some time. The fused mass was treated with dilute ammonia, and the solution filtered after standing for several days.

After adding double the amount of ammonium sulphite necessary to precipitate the solution of silver (which contained less than 2 per cent. of the metal), and allowing it to remain in closed vessels filled up to the neck, very nearly the whole of the silver was precipitated in beautiful crystals, having apparently the form of hexagonal pyramids (in reality tesseral). The remainder of the silver was thrown down on heating the solution. The precipitation is complete, the total loss amounting to about 0·5 per cent. After washing, the silver was placed in contact with strong ammonia, and digested in a closed flask for many weeks. On evaporating the solution, a *non-explosive* black substance was obtained, which on treatment with hydrochloric acid gave silver chloride. The filtrate from the latter contained a small quantity of copper, amounting, as found by colorimetric estimation, to about 0·0002 per cent. of the silver employed.

The silver was then fused in the usual way with borax and nitre, poured into a mould made of kaolin, the bars treated with fusing potassium sodium carbonate, and washed successively with boiling hydrochloric acid and ammonia. One portion was distilled in a furnace made entirely of lime, but only a small quantity was thus obtained from want of a platinum blowpipe, one made of hard *glass* having been used. Another portion which served for the atomic weight determination, was fused in a furnace made of lime, and granulated by pouring from a considerable height into distilled water.

The colour of this silver was beautifully white, and its standard fineness is, according to Stas = 99.997, the distilled silver being = 100.000.

*On the Occlusion of Oxygen in Silver of M. Stas.*

Dumas (*Ann. Chim. Phys.* [5], 15, 289—304), as is generally known, found that silver—which had been hitherto regarded as pure—when heated in a Sprengel vacuum gave up considerable quantities of oxygen, so that the standard fineness becomes 99.992 to 99.975 instead of 100, according as to whether 57 up to 174 c.c. of occluded oxygen = 0.008 to 0.025 per cent. by weight are given up by 1 kilo. of the metal.

This circumstance is theoretically of the highest importance, silver being in reality the standard of the atomic weight determinations of Stas, and consequently of many others depending upon these. But if the silver used by Stas had not been pure, the atomic weight of silver would be only  $\text{Ag} = 107.929$  instead of 107.938 (Ostwald's number) or even only  $\text{Ag} = 107.911$ , according to the amount of oxygen, the maximum difference amounting to 0.027. In the same way the whole of Stas's numbers will be affected, and, indeed, Mallet (*Phil. Trans.*, 1880, 1003; *Chem. News*, 45 and 46) and Clarke ("Recalculation of the Atomic Weights," 262) applied this "Dumas Correction" to the numbers obtained by Stas. But certainly Sebelien ("Beiträge zur Geschichte der Atomgewichte," 90) is right in remarking: "Eine Correction der Stas'schen Zahlen einführen zu wollen hiesse nur dessen classisches Werk verderben, ohne Garantie dafür erhalten zu haben, der Wahrheit näher gekommen zu sein."

Mallet (*loc. cit.*) prepared his pure silver by a method slightly different from that of Stas, and on heating it in a Sprengel vacuum he obtained for 1000 grams of silver 34.63 to 30.12 c.c. of a gas. The silver was placed on a layer of lime, and the gas does not seem to have been analysed, being taken by Mallet for oxygen without any remark. The only chemist who has in this respect investigated silver prepared by Stas's method was J. D. van der Plaats ("Mand-

blad voor Natuurwetenschappen," 1886, No. 2, blz. 25–32). He gives the full history and literature of this subject, and finds that pure silver does not change its weight when heated in a current of air, hydrogen, or carbon monoxide. On heating in a Sprengel vacuum, no loss of weight took place, but from 10 grams of the metal as much as 2 c.c. of a gas were obtained, this being regarded by the author as air, for 0.5 c.c. were absorbed by phosphorus. It is to be regretted that only 10 grams of silver were employed in this beautiful research, for, calculated for 1000 grams of silver, the above quantity becomes 200 c.c. of gas, and is therefore larger than the maximum obtained by Dumas. Van der Plaats concludes with the following interesting passage: "Enkele weken geleden vernam ik echter, hoe Dumas voor zijn dood de overtuiging heeft verkregen, dat door zijne proeven de aanwezigheid van zuurstof in zilver niet bewezen is."

In order to settle that interesting question, I have investigated the bars of silver prepared by Stas's second method. I constructed a Sprengel air-pump, provided with a system of air-traps, in order to avoid the mercury carrying air with it; the single parts of the apparatus were, of course, fused together, or, when Bohemian glass had to be connected with soft Thuringian glass, mercury joints were used. (See S. P. Thompson,\* "The Development of the Mercury Air-Pump," London, 1887 and 1888.)

In the preliminary experiments, about 3 c.c. of a gas—air—were obtained for every 100 grams of silver, but it was found later on that this was due to surface condensations and to moisture. It was therefore necessary to insert between the pump and the tube containing the silver a U-tube filled with pumice stone containing sulphuric acid. (Phosphorus pentoxide was not used, as it was found to contain some trioxide, the vapour of which might contaminate the silver.)

*Experiment 32* was carried on with all possible care. For this purpose, 153.2133 grams of pure silver in bars was heated nearly to its melting point, and, after cooling, placed in a combustion tube of the hardest Bohemian glass, made for this purpose at the celebrated works of J. Kavalier (Sázava). The inner diameter of the tube was 19 mm., the walls were of 2.2 mm. thickness, and the end, which was not connected with the air-pump, was drawn out conically. In the first place the silver contained in the tube was heated at 150°, while a current of carefully dried and purified air was drawn over it, and as soon as it was cold the tube was sealed up at the conical end. A vacuum was then made in the tube, and the next day it was again pumped out.

When a vacuum as perfect as possible was established, the tube

\* I am indebted to the author for the copy of this most interesting paper.

containing the silver was heated to  $450^{\circ}$ , the pump acting all the time, and the gas given off was collected in a carefully graduated microendimeter, 1 mm. of the scale of which corresponded to 0.076 c.c., so that, by means of a telescope, the volume of the gas could be read to within about  $\pm 0.004$  c.c. The volume of the gas collected was 0.219 c.c. at  $0^{\circ}$  and 760 mm.\* The microendimeter was now replaced by a fresh one, and the temperature raised to the strongest red heat which could be applied to the tube without its form changing, and the tube was pumped out at this temperature during six hours. (This is the duration of Dumas' experiment, but it was far longer than was necessary for my purpose.) The volume of gas given off between  $450^{\circ}$  and a red heat was found to be = 0.844 c.c.

It was possible to analyse this small quantity of gas very accurately by Bunsen's method, using the microendimeters mentioned above, and in this way it was found to consist of 0.586 c.c. of oxygen and 0.298 c.c. of nitrogen, the latter value corresponding to 0.312 c.c. of air, so that the quantity of oxygen given up by the silver at a red heat amounts to 0.532 c.c.

*Experiment 33.*—In order to apply a correction to the very small volumes of gas in question, it was necessary to study the way in which my "Sprengel vacuum" behaves on heating. An experiment identical with the foregoing was therefore made, using an *empty* glass tube, under perfectly similar conditions. The volume of the gas collected was = 0.249 c.c.

*Experiment 34* was made with the silver which had been heated at  $150^{\circ}$  as above in Experiment 32, and then to a red heat. The volume of the gas was = 0.215 c.c. (air). Experiment 34 gave 0.215, Experiment 33 gave 0.249, Experiment 32 gave 0.219 up to  $450^{\circ}$ . These three quantities are identical, so that the last one is not to be accounted for in Experiment 32.

The net result is that 153.2133 grams of silver when heated to redness in a Sprengel vacuum give off 0.312 c.c. of air, probably condensed, and 0.524 c.c. of oxygen. Its weight is 0.0007609 gram = 0.0004996 per cent., so that the composition of the silver in question is—

Silver . . . . .	99.9995
Oxygen . . . . .	0.0005
	<hr/>
	100.0000

The same silver, according to Stas, has a standard fineness of 99.997, that of distilled silver being 100.000; and that of the least

\* All volumes given below are reduced to normal temperature and pressure.



pure silver of Stas being 99.994. In these two cases, the differences between the samples of purest silver are, therefore, 6 to 12 times larger than that due to the "occlusion" of oxygen. The last-named impurity cannot be determined either by titration or by the change of weight before and after heating, since small traces of silver are volatilised and condensed in the colder part of the tube. Moreover, some mercury vapour may become condensed in the hot silver on cooling, so that, before using it for the atomic weight determinations, it must be remelted in a lime crucible and poured into water.

But, as the very slight impurities of the undistilled silver of Stas, amounting to 0.003—0.006 per cent., were not regarded in his fundamental researches, the silver prepared by his methods having been declared by Stas as "absolutely pure," it is seen that the classical researches of Stas, which will for ever remain a model of exact investigation, *do not require the correction proposed by Dumas, due to an occlusion of oxygen in silver, its quantity being practically nought.*

I feel convinced that the distilled silver gives *absolutely no oxygen* when heated in a vacuum, the very small amount found by me being due to some otherwise inappreciable impurity contained in my silver.

#### *Determinations of Bromine in Tellurium Tetrabromide.*

The tetrabromide obtained by sublimation in a vacuum was weighed, as above stated, most exactly, and dissolved in the same vessel in two to four times its weight of a solution of 1 part of pure tartaric acid in 1 part of water. Then, from Experiment 31, the quantity of silver necessary for the complete precipitation of the bromine, was calculated and weighed out most exactly, and dissolved in about five times its weight of nitric acid of sp. gr. 1.24, either in the apparatus, Fig. 1, or in the flask in which the precipitation had to be effected. These vessels were Gay-Lussac's silver test-flasks of 200—500 c.c. capacity but equal diameter. They could be closed with tightly ground and carefully polished stoppers, having a sharp cone at their lower part projecting into the flask, this causing a quicker division of the flocks of silver bromide on agitation. The agitation was effected by means of the apparatus seen in Fig. 6, which could be set in action by a water engine *a, b, c*. The flask *f* is contained in a layer of black cloth and in a tightly closed box, *e*, suspended by an elastic rubber spring, *g*. The agitation must be continued for many hours, not only for clearing the liquid, which takes place in a few minutes, but because the silver bromide gives up its impurities, especially tellurium, only when the flocculent precipitate has been entirely converted into the pulverulent modification.

After clearing, the *very small* excess of silver or bromine present in the liquid was determined by standard decinormal solutions. The

FIG. 6.



silver solution used for this purpose was prepared by dissolving 1 gram of pure silver in nitric acid and making up to 1 litre with water distilled over alkaline permanganate. The potassium bromide solution was prepared by dissolving 1.10340 grams of pure potassium bromide in water and making up to 1 litre. The bromide was prepared from the purest medicinal preparation by evaporating its solution to dryness with *pure* bromine and then fractionally dissolving in water and recrystallising. (See Krüss, *Annalen*, **238**, 241.) Before weighing, it was heated to redness in a double platinum crucible.

The titration was effected by means of carefully graduated narrow pipettes, open at their lower end and closed at the top by a rubber

tube, on opening which and letting air in carefully, the liquid can be allowed to drop out without coming into contact with greased stopcocks. The operation was effected in a perfectly dark room, but the liquid to be tested was lighted by a beam of *yellow* light. *The light must contain chemically active rays*, otherwise the slight turbidities become invisible. Red light—in general light of less than  $\lambda = 550$ —does not answer the purpose. If large quantities of the standard solutions are added, slight decomposition of the silver bromide takes place, so that the limit of complete precipitation changes in such a way that after some time the liquid again yields a precipitate with silver solution. This is completely avoided in my case, the volume of the standard solution to be added amounting to a *few drops only*, and being sometimes nought.

In this way the following experiments were made, every one of which required several days for completion.

Exp. No.	TeBr. grams.	Ag. grams.	Br. p.c.	Atomic weight.
35. ....	2.14365	2.06844	71.483	127.60
36. ....	1.76744	1.70531	71.478	127.63
37. ....	1.47655	1.42477	71.484	127.59
38. ....	1.23354	1.19019	71.479	127.63
Mean. ....			71.481	127.61

From these experiments it is seen that the number representing the atomic weight of tellurium is  $\text{Te} = 127.61$ , this number being *larger by 0.75* than the atomic weight of iodine!

Indeed, from a purely experimental point of view, the present work may be regarded as completed, and 20 years ago no one would have doubted that tellurium now belongs to those elements, the atomic weight of which is very exactly determined.

This is, however, not the case when we regard the matter in the light of chemical philosophy, for tellurium with such an atomic weight would be a striking exception to the periodic law, being in fact the first element the properties of which are *not* a function of its atomic weight!

This anomaly might, however, be only apparent, and might be possibly explained in one of the following ways:—

(a.) *The Atomic Weight is badly Determined.*—Such an assumption is impossible, the determinations, carried on volumetrically (Experiment 35—38), agreeing completely with the gravimetric determination, so that an error of *four units* ( $127.6 - 123.6 = 4.0$ ) cannot be assumed to have taken place, such an error being 200 times as large as the largest deviation from the mean  $= \pm 0.02$ .

(b.) *The Bromide may contain some Oxybromide.*—This was very improbable, as the metal and the bromide were obtained by sublimation. The absence of oxygen in the bromide was shown by complete analysis.

*Experiment 39.*—4.4392 grams of tellurium tetrabromide were dissolved in hydrochloric acid and precipitated by sulphurous acid. The tellurium was collected by reversed filtration. In this way 1.2764 grams = 28.75 per cent. of tellurium was obtained. The result is slightly high on account of an unavoidable admixture of tellurium dibromide.

*Experiment 40.*—3.6247 grams of tetrabromide were reduced with sulphurous acid and the tellurium heated in the flask in a current of hydrogen at 200°, hydrobromic acid being found to escape. In this way, 1.0350 grams of pure tellurium was obtained = 28.55 per cent.

From this and the Experiments 35—38, therefore, the composition of tellurium tetrabromide becomes:—

Tellurium .....	28.55
Bromine .....	71.48
	<hr/>
Total .....	100.03

Tellurium tetrabromide contains no oxygen and consequently no oxybromide.

(c.) The following is the third possible explanation. *Tellurium is not a homogeneous body*, but contains an admixture of foreign substances which have a higher equivalent than the bromine equivalent of tellurium. (This equals  $127.6 \div 4 = 31.9$ , but ought to be about = 31.) These admixtures might be partly known elements such as Se (equivalent from  $\text{SeBr}_2 = 39.5$ ), Sb (eq. = 40), Bi (eq. = 69.3), and partly hitherto unknown elements of the same natural group as Mendeléeff's dwiselenium = 166 and dwitellurium = 214. Some of their properties may be predicted from their position in the periodic system.

Before assuming that tellurium forms a striking exception to the periodic law, and that this law consequently loses a great deal, if not all, of its authority. I have thoroughly investigated the question as to whether tellurium is a complex substance or not. For, if the periodic law is true, we may conclude by *deduction*\* that tellurium contains a foreign substance which renders its "atomic weight" higher.

\* Applying the periodic law, the author showed by the process of *deduction eleven years ago* that the atomic weight of beryllium is not  $\text{Be}''' = 13.6$ , as was assumed by Nilson and Pettersson, but  $\text{Be}'' = 9.1$ , in spite of its low specific heat, just as the existence of the simple molecules  $\text{AlCl}_3$ , &c., has been foreseen. It is remarkable that the author's paper on this subject was *not* mentioned by Nilson

*Attempts to Decompose Tellurium.*

An attempt to decompose the metal by fractional distillation gave no results in the hands of Wills (*loc. cit.*).

*First Method.*—Tellurium tetrabromide was subjected to fractional sublimation in a vacuum. The more volatile portion gave  $\text{Te} = 127.60$  and  $127.63$  (see Experiment 35 and 36); the less volatile portion  $\text{Te} = 127.59$  and  $127.63$  (Experiments 37 and 38).

*Second Method.*—A considerable quantity of crude tellurium was dissolved and precipitated by sulphurous acid. The tellurium obtained was fused in many portions with potassium cyanide, and the claret-coloured solution was precipitated fractionally by passing in a current of air.

The single portions of tellurium obtained were distilled in a current of hydrogen and converted into the bromide, which was most carefully analysed as above.

Exp. No.	Fraction No.	$\text{TeBr}_4$ grams.	$\text{Ag}_4$ grams.	Br. p. c.	Atomic weight.
39. ....	I.	3.07912	2.97064	71.472	127.67
40. ....	I.	5.47446	5.28157	71.472	127.67
41. ....	II.	3.30927	3.19313	71.482	127.60
42. ....	IV.	7.26981	7.01414	71.477	127.64
43. ....	IV.	3.52077	3.39667	71.471	127.67
Mean . . . . .					127.65

The experiments agree so remarkably that the concordance could not be closer if the tellurium were absolutely homogeneous; the largest deviation from the mean falling *almost* within the unavoidable experimental errors.\*

*Experiment 44.*—For applying the correction for weighing in a vacuum, the sp. gr. of tellurium tetrabromide was taken in pure anhydrous benzene at  $15^\circ \text{C}$ ., the numbers referring to water = 1 at  $4^\circ \text{C}$ . in a vacuum.

Sp. gr. of benzene . . . . .	0.88456
Weight of tellurium bromide . . . . .	3.40584 gram.
Weight of benzene displaced . . . . .	0.69904 „
Sp. gr. of $\text{TeBr}_4$ at $\frac{15^\circ}{4^\circ}$ . . . . .	4.310

and Pettersson when they had experimentally confirmed both the above suppositions.

\* An error of  $\pm 0.1$  milligram of silver (= two drops of its standard solution) causes, with 1 gram of the substance, a difference in the atomic weight of  $\pm 0.05$ , with 5 grams of substance a difference of  $\pm 0.01$ .

Loss of weight in air of 1 gram (Prague)—

Tellurium tetrabromide .....	0.274
Silver .....	0.112

The atomic weight of tellurium in a vacuum is obtained by adding to the numbers obtained in air +0.07.

*Third Method.*—A hydrochloric solution of pure tellurium dioxide (preparation see under G) was fractionally precipitated with ammonia, and eight fractions were thus obtained.

*Fraction 9* was precipitated from the last filtrate with sulphurous acid in the presence of hydrochloric acid.

*Fraction 10.*—After boiling off the excess of sulphur dioxide, the solution was precipitated with hydrogen sulphide. A brownish-red sulphide was obtained, the small quantity of which did not permit me to ascertain its nature.

The tellurous acid obtained in the single fraction was converted into the element, and this as well as the bromide prepared from it were purified as above by sublimation.

Exp. No.	Fraction No.	TeBr <sub>4</sub> . grams.	Ag <sub>4</sub> . grams.	Br. p. c.	Atomic weight.
45. ....	1.	2.35650	2.27363	71.477	127.64
46. ....	4.	1.51931	1.46564	71.465	127.71
47. ....	9.	1.43985	1.38942	71.488	127.57
Mean .....					127.64

This again would seem to point to an identity of the single fractions.

In the following experiments, the tellurium was only dried and fused in a current of hydrogen, but not distilled. The tetrabromide was only freed from the dibromide by fractional sublimation in a vacuum, but it was not converted into vapour, as it *decomposed* with the formation of a deep-violet vapour and of a large quantity of the greenish-black dibromide. This tetrabromide possessed a peculiar greenish colour, and its solution in tartaric acid was greenish-brown. The substance differs in properties and composition completely from the normal tellurium tetrabromide, as seen from the following experiments:—

Exp. No.	Fraction No.	TeBr <sub>4</sub> . grams.	Ag <sub>4</sub> . grams.	Br. p. c.	Atomic weight.
48. ....	1.	1.85162	1.77858	71.160	129.63
49. ....	2.	1.46740	1.38428	69.886	137.72
50. ....	9.	1.48180	1.42573	71.279	128.88

The results obtained allow us to draw the following remarkable conclusion.

If tellurium, obtained by any process of fractionation whatever, be subjected to distillation in a current of hydrogen, and the tetrabromide be prepared from this by sublimation in a vacuum, its analysis always gives the same atomic weight for tellurium. So that on comparing the quantities of the tetrabromide with those of the corresponding silver, as used in Experiments 35—38, 39—43, and 45—47, the following result is obtained :—

TelBr <sub>4</sub> . grams.	Ag <sub>4</sub> . grams.	Tellurium. Atomic weight.
34.59027	33.37355	<u>127.64</u>
Experiment 46, maximum . . . . .		127.71
„ 47, minimum . . . . .		<u>127.57</u>
Difference . . . . .		0.14
Largest deviation from the mean ..		±0.07
Probable error of the mean result*.		±0.008

If, however, the tellurium be only fused in a current of an indifferent gas, and the tetrabromide be not sublimed, higher numbers will be obtained. In this way in the Experiments 48, 49, and 50 we got  $\text{Te} = 129.63, 137.72, \text{ and } 128.88$ .

The differences are too large to be due to experimental errors, as the difference between 137.72 and  $127.64 = 10.18$  is 144 times larger than the largest deviation from the mean, and 127.2 times as large as the probable error of the mean result. But also in the case of the smallest number, 128.88, the corresponding numbers are 17 and 155 times larger.

It is therefore very probable that on distilling tellurium in a current of hydrogen, and the tetrabromide in a vacuum, one constituent of tellurium escapes partly, the presence of which in the last three cases renders the atomic weight higher.

The fact is a very remarkable one, although it would have been hardly remarkable except for the existence of the periodic law, that in the greater number of cases the “combining weight” (we cannot say atomic weight!) of tellurium remains constant, so that the quantity of matter which takes part in the reactions as “tellurium” weighs 127.6, oxygen weighing 16.

*Tellurium is a true “Gadolinium”† of the hydrogen sulphide group.*

\* Calculated from the formula  $\pm 0.6745 \sqrt{\frac{S}{n(n-1)}}$ , where  $S$  = sum of the squares of the errors,  $n$  = number of experiments; here  $n = 12$ .

† *Compt. rend.*, **103**, 795. The mixture of yttrium, erbium, and ytterbium oxides, showing apparently a constant molecular weight in different minerals, was called “Gadolinium” oxide by Nordenskiöld. Rammelsberg (*Berl. Akad.*, **30**, 549) has shown that this assumption contradicts the result of his analyses.

I. *Analysis of the Dibromide.*

A large amount of time and work was expended on the study and analysis of tellurium dibromide, my aim having been to determine the atomic weight of tellurium by as many independent methods as possible. I expected that the quantity of bromine combined with 100 parts of tellurium in the dibromide, and that in the tetrabromide would stand exactly in the proportion 1 : 2.

The dibromide was prepared by fusing the tetrabromide with an excess of powdered tellurium, and sublimation either in a vacuum or in a current of carbon dioxide,  $\text{TeBr}_4 + \text{Te} = 2\text{TeBr}_2$ . It forms a blackish-green or black crystalline mass, or a black powder, or, after careful sublimation, needles of a pale steel colour. The powder is olive-green, with a yellowish tinge. The appearance, indeed, seems to show that the substance is a mixture either of several allotropic modifications, or of different compounds. On treatment with tartaric acid solution, tellurium tetrabromide dissolves, forming a yellow solution, which, however, is sometimes greenish-brown from the presence of another substance,



The dibromide must be finely powdered under the tartaric acid solution, otherwise some of the dibromide may escape decomposition, as seen from the following.

*Experiment 51.*—1.3856 grams of the dibromide was only extracted with tartaric acid, and the solution gave 1.6730 grams of  $\text{AgBr} = 51.38$  per cent. bromine. The following experiments were made with tellurium dibromide of different preparations. The bromine was determined as silver bromide, which was collected in a dark room by reversed filtration:—

Exp. No.	$\text{TeBr}_2$ . grams.	$\text{AgBr}$ . grams.	Br. p. c.
52. ....	0.5526	0.7160	55.14
53. ....	0.8322	1.0726	54.85
54. ....	2.3741	3.0693	55.02
55. ....	1.00872	1.29556	54.658

After dissolving the insoluble washed residue of tellurium in dilute nitric acid in the apparatus Fig. 1, it was tested for bromine, but silver nitrate gave only a small, flocculent, greyish-violet precipitate, which was neither silver bromide nor silver tellurium tartrate.

The percentage of bromine calculated for  $\text{Te} = 127.64$  in the dibromide ought to be  $\text{Br} = 55.62$ . All the results obtained were lower, the highest (Experiment 52) pointing to an atomic weight of  $\text{Te} = 130$ , the lowest (Experiment 55) to  $\text{Te} = 133$ .



From the analyses of tellurium tetrabromide, dibromide, and the observations regarding them, the following conclusion may be drawn:—

*Tellurium is not a simple substance.*

The question arises, whether the numbers, obtained by the synthesis of the dioxide and the sulphate of tellurium, giving  $\text{Te} = 125\text{--}126$  (see Experiments 1—19), are to be regarded as inaccurate?

This I deny most decidedly. On the contrary, I regard these experiments as another proof of the complex nature of tellurium. For a mixture of several elements—probably three, as seen from the result of the fractionation with ammonia—may be expected to possess an affinity for oxygen different from that which they have for bromine, and indeed, the stability of the mixed bromides obtained from different fractions is very different.

The next task consists in studying the nature of the foreign admixtures of tellurium, in order to prepare pure, real tellurium, *which remains to be discovered*.\*

I should be much obliged to my brother chemists if they would kindly leave this problem to be worked out by me for some time to come, as only now, after six years' labour, have I begun to overcome some of the difficulties connected with the research, and I expect to encounter even more serious ones in the future. Nothing is more hurtful to true science than the hasty publication of incomplete and unverified results, and I hope I may not be forced by circumstances to adopt such a course.

Some of the results, unpublished here, have been communicated by the author to the Chemical Society at the meeting of June 6th, 1889.

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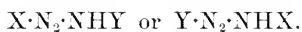
\* The behaviour of acid tellurium solutions towards hydrogen sulphide is another proof of its compound nature. The first drops of sulphuretted hydrogen water cause a reddish-brown coloration of the solution, showing a peculiar fluorescence, due probably to the formation of a colloidal sulphide. On adding some more sulphuretted hydrogen water, a reddish-brown precipitate is thrown down, the solution remaining reddish-brown. As soon as the gas is present in excess, the volume of the sulphide (?) diminishes: it becomes black, and consists now of a mixture of tellurium and sulphur. After extracting the latter with carbon bisulphide, the precipitate still contains several per cent. of sulphur, probably in the form of a sulphide.

XLII.—*The Isomerism of the Alkyl-derivatives of Mixed Diazoamido-compounds.*

By RAPHAEL MELDOLA, F.R.S., and F. W. STREATFEILD, F.I.C.

THE isomerism which has been brought to light in the course of our investigations of the alkyl-diazoamides is, as we have already pointed out in former papers, quite inexplicable by the formula generally assigned to these compounds, and in our last communication on this subject we promised to make this isomerism the subject of further research (Trans., 1888, 664). For the complete appreciation of the nature of the problem which we have taken up, it will be advisable to state once more the general conclusion to which our former work pointed and the principle of the method which we have employed in arriving at this conclusion.

The generalised formula of the diazoamides of mixed type is generally written—



According to this view, two alkyl-derivatives only are possible, viz.:—



When mixed diazoamides are prepared, only one compound can be obtained from any pair of dissimilar amines, Griess having shown that it is immaterial in which order the amines are diazotised and combined, a discovery which has been since confirmed by many investigators. We may add that we have made numerous experiments in the course of our work with many pairs of dissimilar amines, and have invariably obtained the same compound in whichever order the amines were diazotised and combined, so that there can be no doubt as to the generality of Griess's conclusions.

The diazoamides, both normal and mixed, can be readily alkylated by heating them in alcoholic solution with the theoretical proportions of alkyl iodide and potassium hydroxide.

Alkyl-derivatives can also be prepared by acting with a diazotised amine upon an alkylamine, such, for example, as by the action of  $X \cdot N_2 \cdot Cl$  on  $Y \cdot NHR'$  or of  $Y \cdot N_2 \cdot Cl$  on  $X \cdot NHR'$ . Our first experiments were undertaken with the object of determining the constitution of the mixed diazoamides by comparing their directly alkylated derivatives with the two alkyl-derivatives prepared from the corresponding amine and alkylamine as above. It was found that the derivative prepared by direct alkylation corresponded with neither of

the other isomerides, and it was accordingly inferred that any pair of aromatic amines could give rise to the three isomeric alkyl-diazo-amides:—

1. By the action of  $X \cdot N_2 \cdot Cl$  on  $Y \cdot NHR'$ .
2. By the action of  $Y \cdot N_2 \cdot Cl$  on  $X \cdot NHR'$ .
3. By the action of  $KOH$  and  $R''$  on  $X \cdot N_3H \cdot Y$ .

The generality of this conclusion has hitherto rested only on the two cases made known in former papers, viz., the methyl- and ethyl-derivatives of the diazoamides obtained from para- and meta-nitraniline. In the present paper, we give the results of the extension of our experiments to many other pairs of amines, and the truth of our former inference is, as will be seen, completely borne out in every case. From each pair of amines experimented with, we have obtained three isomeric alkyl-derivatives. These series of three isomerides are referred to in the paper as triplets. The compounds produced by Methods 1 and 2 (see above) are easily prepared, and in most instances have presented but little difficulty in the way of purification. The compounds of this class are for the present formulated in accordance with their mode of production on the types  $X \cdot N_2 \cdot NR' \cdot Y$  and  $Y \cdot N_2 \cdot NR' \cdot X$ . The compounds prepared by direct alkylation, which are provisionally formulated on the type  $X \cdot N_3R' \cdot Y$  (Method 3), have been much more difficult to obtain in a state of purity, a difficulty which we attribute entirely to the tendency of the *mixed* diazoamides to become contaminated with traces of the normal diazoamides by secondary reactions occurring during their formation. We are not aware whether other experimenters have experienced a similar difficulty in dealing with these compounds, and on referring to the various papers by previous workers we find that the composition has, in nearly all cases, been considered as settled by the determination of one element only, generally the nitrogen. It will be seen, however, that this mode of procedure cannot be regarded as satisfactory, since a mixed diazoamide containing a halogen-atom in one radicle might be contaminated with an appreciable quantity of the normal compound without affecting the percentage of nitrogen beyond the ordinary limits of experimental error. To give a specific instance: By the action of paradiazotoluene chloride on parachloraniline, or of parachlorodiazobenzene chloride on paratoluidine, there is formed a mixed diazoamide of the formula  $C_6H_4Cl \cdot N_3H \cdot C_7H_7$ , which contains 17.1 per cent. of nitrogen and 14.8 per cent. of chlorine. The corresponding pair of normal compounds would be



(containing 26.7 per cent. of Cl and 15.8 per cent. of N), and

$C_7H_7 \cdot N_3H \cdot C_7H_7$  (containing 18.7 per cent. of N). The two normal compounds differ, therefore, from the mixed compound only by 1.3 and 1.6 per cent. of nitrogen respectively, so that a considerable quantity of one or both the normal compounds might be present in admixture with the mixed diazoamide without being detected by an analysis in which the nitrogen was the only element determined.

From considerations such as the foregoing, it is obvious that the purity of the mixed diazoamides can only be regarded as satisfactorily demonstrated when at least two of the constituent elements are determined. The mixed compounds containing a halogenised radicle on one side of the  $N_3H$ -group are particularly well adapted for showing when a pure product is obtained, because the presence of a small quantity of one or the other of the normal compounds is easily shown on determining the halogen; whereas the nitrogen determination would fail to reveal the presence of a small percentage of such an impurity. For this reason we have made use of parachloraniline or parabromaniline as one of the amines in the preparation of all the mixed diazoamides described in the present paper. It is evident that such compounds are more suitable for the purposes of the investigation upon which we are engaged than the more symmetrical mixed compounds containing such radicles as  $(p)NO_2 \cdot C_6H_4$  and  $(m)NO_2 \cdot C_6H_4$  on each side of the  $N_3H$ -group. Thus the mixed compound,  $(p)NO_2 \cdot C_6H_4 \cdot N_3H \cdot C_6H_4 \cdot NO_2(m)$ , described by us in a former paper, would have the same percentage composition as the two normal compounds,

$(p)NO_2 \cdot C_6H_4 \cdot N_3H \cdot C_6H_4 \cdot NO_2(p)$  and  $(m)NO_2 \cdot C_6H_4 \cdot N_3H \cdot C_6H_4 \cdot NO_2(m)$ , either or both of which might be present in admixture with the mixed parametadinitro-compound without being capable of detection by analysis. It was only after considerable experience with the mixed compound containing one halogenised radicle had shown us that varying quantities of one or the other of the corresponding normal compounds were generally formed at the same time as the mixed diazoamide, that we were led to discredit the purity of those mixed compounds prepared by previous investigators, and taken as pure on the strength of a nitrogen determination only. For the same reason we were led to suspect that our own preparations of the mixed para-metadinitrodiazoamidobenzene might have been contaminated with more or less of the normal dipara- or dimeta-nitro-compound, analysis being obviously of no avail for the decision of this question. We have, therefore, submitted the mixed dinitrodiazoamide from paranitraniline and metanitraniline to a further critical examination, in order to clear up this point in the first place, slight variations in the melting points of different preparations having con-

vinced us, in the light of more recent experience, that traces of the normal compound might have been present in our earlier experiments. We shall describe the results of these experiments before passing on to the other triplets. With respect to the melting points of the diazoamido-compounds and their alkyl-derivatives, it will be necessary at this stage of our work to offer some general observations.

Starting from the fact, which we now regard as established on a fairly wide basis, that each pair of amines gives rise to three isomeric alkyl-diazoamides, we have found that the melting point of the compound produced by direct alkylation is always more vague than that of either of its isomerides. This vagueness of melting point appears to be a natural property of the compounds of this series. The explanation of this property is to be found in the fact that the diazo-amides, as well as their alkyl-derivatives, are all more or less prone to decompose, with evolution of nitrogen, on heating; so that the melting point is, in most cases, also the point of decomposition, and it is well known that under such circumstances sharpness of melting point cannot be expected. The products formed by direct alkylation, taken as a whole, are more easily decomposable than their isomerides, both on heating and by the action of acids; and it is this fact which accounts for the wider range of their melting points. The instability is more pronounced in those compounds which contain acid radicles, such as  $\text{NO}_2$ , Br, Cl, &c., in both nuclei, and in some of these cases the substance begins to shrink and soften many degrees before fusing to a clear liquid, bubbles of nitrogen being given off more and more freely as the temperature rises. It must be understood that this property more especially pertains to the compounds produced by direct alkylation: the isomerides formed by the action of diazotised amines on alkylamines have fairly sharp melting points owing to their being more stable under the influence of heat. We had noticed this vagueness of melting point in the directly alkylated products of the mixed para-metadinitro-diazo-compound first studied, but we were not aware till we had prepared many analogous compounds that the property in question was characteristic of all the alkyl-derivatives produced in a similar manner.

*Further Experiments to test the Chemical Individuality of Para-metadinitro-diazoamidobenzene and its Alkyl-derivatives.*

*Experiment I.*—Metanitriline was diazotised and combined with paranitriline in the usual manner. The crude product when dry had a melting point of about  $200\text{--}201^\circ$ . On crystallising from alcohol, the following melting points were observed:—

After 1st crystallisation: m. p. 216·5—217°			
„ 2nd	„	„	217°
„ 3rd	„	„	211—212°
„ 4th	„	„	212—212·5°.

The melting point after this remained constant, and we believe this to be about the true point of fusion of the substance, the higher readings of the first and second crystallisations being possibly due to the presence of some of the normal compound,



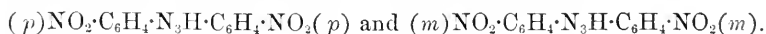
which was removed by the continued crystallisations. As illustrating the difficulty of determining the melting point—even in the case of this compound, which fuses much more sharply than its alkyl-derivatives—we may add that the rate at which the sulphuric acid bath is heated materially influences the result. By causing the mercury of the thermometer to rise very rapidly, the melting point of the compound could be raised to 222° or 227—228°.

*Experiment II.*—In the next experiment, the order of combination was reversed; paranitraniline was diazotised and then combined with metanitriline as before. The crude product when dry fused at about 210—211°.

After 1st crystallisation: m. p. 210—210·5°			
„ 2nd	„	„	212—213
„ 3rd	„	„	211—212·5
„ 4th	„	„	212·5—213·5°
„ 5th	„	„	212·5—213° (constant).

From this result it appears that a purer product was obtained in the first place by this order of mixing. The final products from each experiment were compared and found to be identical in all respects, dissolving in alcoholic potash with the orange-red colour intermediate between the orange solution of the dimetadinitro-compound and the magenta-red solution of the diparadinitro-compound in the same solvent. This pair of experiments serves to show that the para-metadinitro-compound is a distinct chemical substance having a melting point of 212—213°.\*

*Experiment IV.*—The next experiment is a repetition of a former attempt (this Journ., Trans., 1887, 440, note) to synthesise the parameta-compound by mixing the two normal isomerides—



2 grams of each were completely dissolved in alcoholic soda, the solution diluted with water, and then just neutralised with acetic acid so

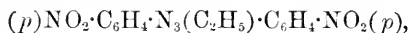
\* In our former papers we gave the melting point as 211°.

as to throw out the diazoamides in a state of perfect admixture. The precipitate, after being collected and washed with water, was crystallised from alcohol, the first crop of crystals being filtered off as soon as the solution was cool. The melting point of this first crop was  $214-215^{\circ}$ , and a second crystallisation brought the melting point up to  $222-223^{\circ}$ —that is, to that of the pure diparadinitro-compound. The mother-liquor from the first crop deposited a second crop of crystals on standing. These had a melting point of  $193-194^{\circ}$ , and thus proved to be the dimetadinitro-compound. The two normal compounds do not, therefore, enter into combination, and are easily separable by fractional crystallisation.

*Experiment V.*—3 grams of each of the two normal isomerides were mixed and dissolved in alcohol with the theoretical quantity of potassium hydroxide (one molecular proportion) and ethyl iodide. The mixed compounds were ethylated by cohobation in the usual way. The product, after being collected and washed with water had, when dry, a melting point of  $141-166^{\circ}$ , and was seen under the microscope to consist of a mixture of two kinds of crystals. The ethyl-derivatives were then crystallised from alcohol.

After 1st crystallisation: m. p. $150-179^{\circ}$			
„	2nd	„	„ $188-191.5$
„	3rd	„	„ $191-192^{\circ}$ (constant).

The result shows that no combination of the ethyl-derivatives takes place. The normal ethyl-derivative,



being much less soluble than the dimeta-compound, is easily separable from the mixture in a state of purity after three crystallisations.

*Experiment VI.*—The last experiment having shown that alkyl-diazoamides of different solubilities are easily separable by continued crystallisation, a pure specimen of the mixed para-metadinitrodiazo-compound was prepared by combining diazotised metanitriline with paranitriline and crystallising the product from alcohol till the melting point was constant ( $212-213^{\circ}$ ). The purified compound was then ethylated as usual, and the ethyl-derivative crystallised from alcohol:—

After 1st crystallisation: m. p. $151-155^{\circ}$			
„	2nd	„	„ $151-155$
„	3rd	„	„ $151-155$

The substance is thus unresolved by crystallisation from alcohol, and there can be but little doubt as to its chemical individuality.

*Experiment VII.*—Another specimen of the mixed parameta-com-

pound was prepared by combining diazotised paranitraniline with metanitraniline, and the purified product was ethylated as in the last experiment. The ethyl-derivative was then crystallised from alcohol:—

After 1st crystallisation: m. p. 153·5—156°			
„	2nd	„	„ 153·5—156
„	3rd	„	„ 151—153°
„	4th	„	„ 152—156
„	5th	„	„ 152—155

These experiments furnish additional evidence of the identity of the mixed diazoamide prepared by the two orders of combination. The melting point of the ethyl-derivative may be taken as about 151—155°, the vagueness arising from the decomposition of the substance and the consequent difficulty of determining the precise point at which it begins to fuse and the point at which fusion may be said to be complete. We consider the melting point now given as nearer the truth than that given in our earlier papers (148°), our former preparation being probably contaminated with slight traces of one or both of the normal dinitrodiazoamides, the presence of which would, as already explained, escape detection by analysis.

In the following descriptions of the new series of alkyl-diazoamides, we have not thought it necessary in all cases to isolate the mixed diazoamide in a state of chemical purity previous to its alkylation, as it was generally found more expeditious to alkylate the crude product, and then purify the latter by crystallisation. This method of working offers many advantages, because the alkyl-derivatives are in most cases more stable when treated with the solvent than the unalkylated mixed diazoamide. We have, indeed, reason to believe that some of the more unstable mixed compounds, even when pure at starting, may become contaminated with more or less of the corresponding normal compounds on prolonged boiling with alcohol. This point is at present undergoing further investigation, but the results are not as yet ripe for publication. The products of decomposition by hydrochloric acid have throughout been determined by the method described in former papers (Trans., 1887, 438, and 1888, 675.)

# I. THE TRIPLET FROM PARANITRANILINE AND PARABROMANILINE CONTAINING METHYL.

1. *Action of Diazotised Paranitraniline on Methylparabromaniline.*—Paranitraniline was diazotised, and the solution mixed with the theoretical quantity of methylparabromaniline oxalate\* dissolved in

\* This salt was used because of the readiness with which it crystallises, and the



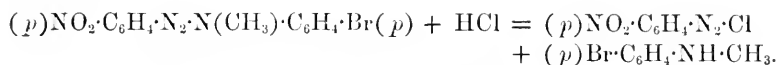
cold water. As soon as the solutions are mixed, an orange resinous substance separates out, and after being allowed to stand for some hours this was collected, washed with cold water, and purified by two or three crystallisations from alcohol. The substance forms minute orange needles melting sharply at  $151-151.5$ .

0.0829 gram gave 12 c.c. moist N at  $13.5^{\circ}$  C. and 744.8 mm. bar.

0.0905           ,,           0.0497 gram AgBr.

	Calculated for (p)NO <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> ·N <sub>2</sub> ·N(CH <sub>3</sub> )·C <sub>6</sub> H <sub>4</sub> ·Br(p).	Found.
N .....	16.72	16.72
Br .....	23.88	23.37

*Decomposition by Hydrochloric Acid.*—0.3267 gram of the substance, allowed to stand for two days under 10 c.c. of strong acid, dissolved with the exception of a trace (weighing 0.0058 gram). The solution on dilution and filtering into an alkaline solution of  $\beta$ -naphthol gave 0.2787 gram pure azonaphthol compound, corresponding to a yield of 86.85 per cent. Theory requires 87.46 per cent. The azonaphthol-compound after crystallisation from glacial acetic acid was identified as paranitrobenzeneazo- $\beta$ -naphthol (m. p.  $249^{\circ}$ ). The decomposition therefore takes place as shown in the equation—



2. *Action of Diazotised Parabromaniline on Methylparanitraniline.*—Owing to the feebly basic property of methylparanitraniline, this combination could not be effected in aqueous solution, as too much acid is required to keep the methylnitraniline dissolved, and the addition of the aqueous solution of diazobromobenzene chloride simply throws out the methylnitraniline in a crystalline unaltered condition. The latter was therefore dissolved in a large volume of cold alcohol, and the diazo-chloride solution slowly mixed; excess of sodium acetate was then added, and the solution allowed to stand for some hours in the cold.\* The dense, orange, crystalline precipitate was collected, washed with water, and crystallised three or four times from boiling alcohol, in which the compound is but very sparingly soluble. It forms small, yellowish, ill-defined crystals melting at  $163-164^{\circ}$  with decomposition:—

facility which it thus offers for obtaining the secondary amine in a solid weighable form, and in a condition of perfect purity.

\* In preparing mixed alkyl-diazo-amides by this method, we have always noticed the production of an odour resembling that of the isocyanides.

0.1210 gram gave 16.9 c.c. moist N at 12.5° C. and 761.2 mm. bar.

0.2769           ,,           0.1547 gram AgBr.

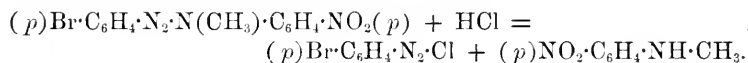
	Calculated for ( <i>p</i> )Br·C <sub>6</sub> H <sub>4</sub> ·N <sub>2</sub> ·N(CH <sub>3</sub> )·C <sub>6</sub> H <sub>3</sub> ·NO <sub>2</sub> ( <i>p</i> ).	Found.
N .....	16.72	16.57
Br .....	23.88	23.77

*Decomposition by Hydrochloric Acid.*—0.3610 gram (less 0.0308 gram residue) decomposed by 10 c.c. strong acid, acting at the ordinary atmospheric temperature for 24 hours, gave 0.3370 gram azonaphthol-compound, corresponding to 102 per cent. Theory requires 97.6 per cent. The azonaphthol-compound on crystallisation from alcohol proved to be *parabromobenzeneazo-β-naphthol*. This last compound does not appear to have been described. It forms deep red needles melting at 168—170°:—

0.2090 gram gave 0.1216 gram AgBr.

	Calculated for Br·C <sub>6</sub> H <sub>4</sub> ·N <sub>2</sub> ·C <sub>10</sub> H <sub>6</sub> ·OH.	Found.
Br .....	24.46	24.75

The decomposition accordingly takes place as follows:—



3. *Methylation of Paranitroparabromodiazamidobenzene.*—Considerable difficulty was experienced in obtaining a specimen of this compound sufficiently pure for methylation, the product generally being contaminated with some of the dinitrodiazamidobenzene, and the nitrogen coming out too high in consequence. In the case of this compound, the nitrogen determination obviously furnishes the most certain criterion of purity. The action of diazotised bromaniline on paranitraniline dissolved in alcohol gave very unsatisfactory results, but the reverse order of combination gave a purer product when the proper precautions were observed. The bromaniline is first dissolved in dilute hydrochloric acid, and then thrown out in a very finely divided state by the addition of sodium acetate, a sufficient quantity of this salt being added to insure the absence of free hydrochloric acid when the whole of the diazo-chloride solution is added. The paranitraniline is diazotised in the usual way, and the solution allowed to drop slowly with constant stirring into the bromaniline suspended in the well-cooled sodium acetate solution. After being allowed to stand for some hours, the orange precipitate is collected, washed with water, and crystallised from alcohol. The substance appears to be capable of crystallising in two distinct forms; if the

crystals separate out rapidly, they consist of orange scales glistening with prismatic colours. By slow crystallisation, the compound is obtained in the form of dense orange prisms with pointed extremities. In most cases the two kinds of crystals were obtained in admixture. The melting point is unfortunately too vague to enable us to state whether this difference of crystalline form indicates the existence of chemical isomerides, as both scales and prisms decompose on heating, and have the wide range of melting point so characteristic of the unstable diazoamides. The melting point ranged from  $175-181^{\circ}$ .\* The prismatic crystals melt somewhat more sharply than the scales, and, no doubt, represent a form of the compound analogous to that assumed by the corresponding mixed diazoamide from paranitraniline and parachloraniline described in our last communication on this subject (*Trans.*, 1888, 673). From the fact that both kinds of crystals give on alkylation the same and apparently a homogeneous compound, we are disposed to believe that there is no chemical isomerism associated with this difference of form. A nitrogen determination in a specimen containing the two crystalline modifications, which it was found impossible to separate completely from one another, gave the following result:—

0.1841 gram gave 27.3 c.c. moist N at  $14^{\circ}$  C. and 759.9 mm. bar.

	Calculated for ( <i>p</i> )NO <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> ·N <sub>3</sub> H·C <sub>6</sub> H <sub>4</sub> ·Br( <i>p</i> ).	Found.
N .....	17.44	17.49

The foregoing compound is very similar in its properties to the corresponding dinitrodiazoamide, dissolving with a red colour in hot, aqueous caustic soda, and with a similar colour in cold alcoholic soda. Methylation was effected in the usual way, by cohobation in alcoholic solution with the theoretical quantities of potassium hydroxide and methyl iodide. The product was purified by repeated crystallisation from alcohol made alkaline with caustic soda (to remove any unmethylated product), and finally from ordinary alcohol. The pure substance forms microscopic yellow needles melting at  $150.5-151.5^{\circ}$ , at the same time frothing up and decomposing.

0.0928 gram gave 12.9 c.c. moist N at  $10^{\circ}$  C. and 769.2 mm. bar.

0.0736       ,,       0.0411 gram AgBr.

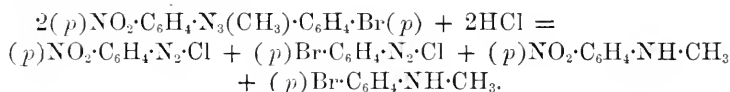
	Calculated for ( <i>p</i> )NO <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> ·N <sub>3</sub> (CH <sub>3</sub> )·C <sub>6</sub> H <sub>4</sub> ·Br( <i>p</i> ).	Found.
N .....	16.72	16.84
Br.....	23.88	23.77

\* The melting point when crystallised from benzene is, according to Goldschmidt,  $184^{\circ}$  (*Ber.*, 1888, 2574). By running up the temperature very rapidly, our preparation could be raised in melting point to about  $187^{\circ}$ .

*Decomposition by Hydrochloric Acid.*—0.2253 gram, allowed to remain under 10 c.c. of strong acid at the ordinary temperature for 2 to 3 hours, left 0.0280 gram unaltered substance, and gave 0.1874 gram azonaphthol-compound, corresponding to about 95 per cent. The azonaphthol-compound had, when crude, a melting point ranging from 184—207°, and thus proved to be a mixture. By continued crystallisation from glacial acetic acid, the mixture was separated, as shown by the following melting points:—

After 1st crystallisation: m. p. 188—234°			
„	2nd	„	225—235
„	3rd	„	240—243.5°
„	4th	„	246.5—247.5°
„	5th	„	249° (constant).

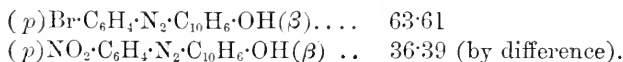
The substance separated is, therefore, paranitrobenzeneazo- $\beta$ -naphthol. The compound accordingly breaks up under the influence of the acid in two ways:—



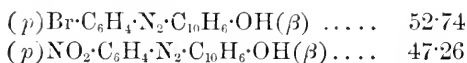
The azonaphthol-compound is thus a mixture of paranitrobenzeneazo- $\beta$ -naphthol and parabromobenzeneazo- $\beta$ -naphthol. If the decomposition took place quantitatively in accordance with the above equation, 100 parts of the diazoamide should yield 92.5 parts of the mixed azonaphthols. Our experiment gave 95 per cent. The 92.5 parts of the mixed azo-naphthols, corresponding to the above decomposition, contain 12.9 per cent. bromine. An analysis of our crude azonaphthol-compound (before fractional crystallisation) gave the following result:—

0.1640 gram gave 0.0600 gram AgBr = 15.56 per cent. Br.

Calculating this bromine as parabromobenzeneazo- $\beta$ -naphthol, the composition of the mixture is accordingly—



If each had been present in molecular proportion, the composition would have been—



From this result it would appear that an excess of parabromodiazazo-

benzene chloride is produced in this decomposition. We shall, however, return to the discussion of this point in a subsequent part of the present paper.

## II. THE TRIPLET FROM PARANITRANILINE AND PARABROMANILINE CONTAINING ETHYL.

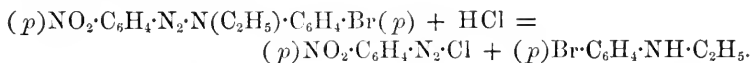
1. *Action of Diazotised Paranitraniline on Ethylparabromaniline.*—The secondary amine was prepared by heating bromaniline with the theoretical quantities of ethyl iodide and sodium hydroxide in alcoholic solution in a flask, with reflux condenser, for about half an hour. The alcohol was distilled off, the oily product washed with water, dissolved in hydrochloric acid, and converted into nitrosamine by the addition of sodium nitrite. When purified by crystallisation from dilute alcohol, the nitrosamine forms lustrous ochreous plates melting at 63–64°. The secondary amine was obtained by reducing the nitrosamine with tin and hydrochloric acid in the usual way. The hydrochloride, which forms dense prismatic crystals, was used for the preparation of the diazoamido-compound. On mixing the solutions of paranitrodiazobenzene chloride and ethylbromaniline hydrochloride, an orange resinous substance slowly separates out on the addition of sodium acetate. After two crystallisations from alcohol, the pure compound was obtained in the form of glistening orange needles melting at 139–140°.

0.0624 gram gave 8.4 c.c. moist N at 12° C. and 767.6 mm. bar.

0.2688 „ 0.1442 gram AgBr.

	Calculated for (p)NO <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> ·N <sub>2</sub> ·N(C <sub>2</sub> H <sub>5</sub> )·C <sub>6</sub> H <sub>4</sub> ·Br(p).	Found.
N .....	16.04	16.14
Br .....	22.92	22.82

*Decomposition by Hydrochloric Acid.*—0.3164 gram, allowed to stand under 10 c.c. strong acid for about four hours at the ordinary temperature, passed completely into solution, and gave 0.2380 gram azonaphthol-compound, corresponding to about 75 per cent. The azonaphthol, after one crystallisation from glacial acetic acid, had the melting point of paranitrobenzeneazo-β-naphthol (249°), indicating the normal decomposition—



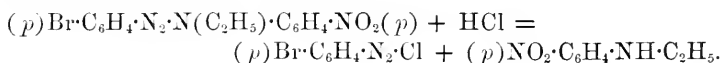
2. *Action of Diazotised Parabromaniline on Ethylparanitraniline.*—Precisely the same difficulty was experienced in bringing about

this combination as in the case of the corresponding methyl-derivative. No combination takes place in aqueous solutions, and the ethyl nitraniline was dissolved in alcohol, and the diazo-chloride solution added as before. The orange crystalline precipitate, which forms under these conditions, consists chiefly of unaltered ethylnitraniline, and contains only a small quantity of the diazoamide sought for. After the precipitate had been collected and washed with water, it was dissolved in alcohol and allowed to crystallise, this operation being repeated till the melting point was constant. Analysis at this stage showed that the substance was still slightly impure (found 15.92 per cent. N and 22.21 per cent. Br), so that the substance was recrystallised from a mixture of benzene and petroleum, and then formed stumpy, yellowish-orange needles melting at 124—125°.

0.1806 gram gave 0.0978 gram AgBr.

	Calculated for	Found.
	$(p)\text{Br}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{N}(\text{C}_2\text{H}_5)\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2(p).$	
Br. ....	22.92	23.04

*Decomposition by Hydrochloric Acid.*—0.2890 gram in 9 c.c. strong acid for two hours at the ordinary temperature left 0.0266 gram unaltered substance, and gave 0.2420 gram azonaphthol-compound, corresponding to 92.22 per cent. Theory requires 93.7 per cent. The azonaphthol once crystallised from glacial acetic acid had a melting point of 168—170°, and proved to be parabromobenzeneazo- $\beta$ -naphthol, indicating the normal decomposition—



3. *Ethylation of Paranitroparabromodiazamidobenzene.*—Instead of attempting to isolate the nitrobromodiazamide in a state of purity, the crude product was dried, and at once ethylated in the usual way. After three crystallisations from alcohol, it was obtained pure in the form of microscopic orange needles melting somewhat sharply at 115—116°.

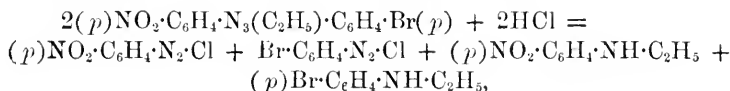
0.1324 gram gave 17.8 c.c. moist N at 12° C. and 758.9 mm. bar.

0.1843           ,,           0.0987 gram AgBr.

	Calculated for	Found.
	$(p)\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_3(\text{C}_2\text{H}_5)\cdot\text{C}_6\text{H}_4\cdot\text{Br}(p).$	
N. ....	16.04	15.93
Br. ....	22.92	22.79

*Decomposition by Hydrochloric Acid.*—In accordance with its comparative sharpness of melting point, this modification was found to be

somewhat more stable under the influence of the acid. 0.3628 gram under 10 c.c. of strong acid, had left a considerable residue after four hours at ordinary temperature, so the contents of the beaker were heated to 30° for a few minutes, and the decomposition then taken as complete. The residue weighed 0.0170 gram, and the azonaphthol 0.3120 gram, corresponding to 90.22 per cent.. The latter in the crude state had a melting point ranging from 153° to 192°, and thus proved to be a mixture. By crystallisation from glacial acetic acid, paranitrobenzeneazo- $\beta$ -naphthol (m.p. 249°) was isolated and identified. If the decomposition took place quantitatively, according to the equation—



100 parts of the diazoamide should yield 88.8 parts of the mixed azonaphthols containing 12.9 per cent of bromine. Analysis of the mixed azonaphthols obtained gave the following results:—

0.2499 gram gave 0.0871 gram AgBr = 14.83 per cent. Br.

This corresponds to a mixture having the following percentage composition:—

$(p)\text{Br}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}(\beta)$ . . . . .	60.62
$(p)\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}(\beta)$ . . . .	39.38 (by difference).

Calculated for equal molecules the result is—

$(p)\text{Br}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}(\beta)$ . . . . .	52.74
$(p)\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}(\beta)$ . . . . .	47.26

In this case also, it appears, therefore, that an excess of parabromodiazobenzene chloride is formed on decomposition.

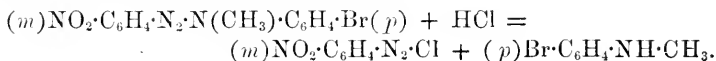
### III. THE TRIPLET FROM METANITRANILINE AND PARABROMANILINE CONTAINING METHYL.

1. *Action of Diazotised Metanitraniline on Methylparabromaniline.*—On mixing the solutions of metanitrodiazobenzene chloride and methylbromaniline oxalate dissolved in water containing enough sodium acetate to decompose the liberated hydrogen chloride, an ochreous crystalline precipitate at once begins to separate. After being allowed to stand for some hours in the cold, the precipitate was collected, washed with water, and purified by crystallisation from alcohol. After four crystallisations, the pure compound was obtained in the form of small, ochreous needles melting sharply at 144°.

0.0801 gram gave 11.5 c.c. moist N at 13.5° C. and 741.5 mm. bar.  
 0.0954        „        13.4        „        „        10°        „        751.6        „  
 0.1130        „        0.0641 gram AgBr.

Calculated for		Found.	
$(m)\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{N}(\text{CH}_3)\cdot\text{C}_6\text{H}_4\cdot\text{Br}(p).$		I.	II.
N .....	16.72	16.50	16.62
Br .....	23.88	24.14	—

*Decomposition by Hydrochloric Acid.*—0.2106 gram, in 7 c.c. strong acid for 20 hours at the ordinary temperature, dissolved with the exception of 0.02 gram and gave 0.1658 gram azonaphthol. The latter when crude had a m. p. of 191—191.5°, and after one crystallisation from glacial acetic acid was identified as metanitrobenzenazo- $\beta$ -naphthol (m. p. 193—194°). The decomposition by acid thus takes place normally as shown in the equation—



The yield of azonaphthol, according to this equation, should be 87.4 per cent. The quantity obtained corresponds to 86.98 per cent.

2. *Action of Diazotised Parabromaniline on Methylmetanitraniline.*—The methylnitraniline was dissolved in a sufficient quantity of dilute hydrochloric acid to keep it in solution in the cold, and the solution of the diazo-chloride added in the usual way. A yellow precipitate at once forms, and after being allowed to stand for some hours the substance was collected, washed, and crystallised from alcohol. Two crystallisations sufficed to render the compound pure in the form of long, slender, yellow needles melting sharply at 160.5—161°.

0.0940 gram gave 13.1 c.c. N at 11.5° C. at 766 mm. bar.

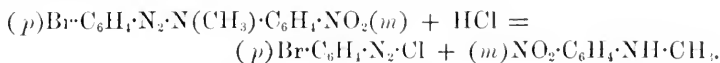
0.1489        „        0.0836 gram AgBr.

	Calculated for	
	$(p)\text{Br}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{N}(\text{CH}_3)\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2(m).$	Found.
N .....	16.72	16.71
Br .....	23.88	23.89

*Decomposition by Hydrochloric Acid.*—0.3411 gram, under 10 c.c. strong acid at the ordinary temperature for 18 hours, dissolved with the exception of 0.0036 gram, and gave 0.3358 gram azonaphthol, corresponding to 99.5 per cent. The theoretical yield is 97.6 per cent. The azonaphthol when crude had a m. p. of 167—170.5°, and was identified, after crystallisation, as pure parabromobenzeneazo- $\beta$ -naphthol.



This diazoamide is therefore decomposed normally by the acid—



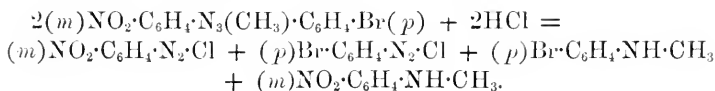
3. *Methylation of Metanitroparabromodiazamidobenzene*.—The compound for methylation was prepared by allowing a solution of meta-nitrodiazobenzene chloride to drop with constant stirring into an emulsion of bromaniline in sodium acetate solution. The product, after being collected, washed, and dried, was methylated by heating with potassium hydroxide and methyl iodide in the usual way. The reaction sets in at once, and the mixture solidified to a pulp of crystals in a few minutes; the methylation was completed by cohobating for half an hour. The product was collected, washed with water, and twice crystallised from alcohol. It then forms slender, yellow needles melting vaguely from 125—137.5°.

0.1001 gram gave 14.1 c.c. moist N at 14° C. and 758 mm. bar.

0.1678 „ „ 0.0942 gram AgBr.

	Calculated for (m)NO <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> ·N <sub>3</sub> (CH <sub>3</sub> )·C <sub>6</sub> H <sub>4</sub> ·Br(p).	Found.
N .....	16.72	16.54
Br.....	23.88	23.89

*Decomposition by Hydrochloric Acid*.—0.2664 gram, under 10 c.c. strong acid for six hours, dissolved completely at ordinary atmospheric temperature, and gave 0.2438 gram azonaphthol, corresponding to 91.5 per cent. The azonaphthol proved, as was anticipated, to be a mixture indicating the decomposition to be—



According to this equation, a yield of 92.5 per cent. of the mixed azonaphthols containing 12.9 per cent. of Br should have been obtained. Our mixed product gave the following result:—

0.2048 gram gave 0.0692 gram AgBr = 14.37 per cent. Br.

This corresponds to—

(p)Br·C <sub>6</sub> H <sub>4</sub> ·N <sub>2</sub> ·C <sub>10</sub> H <sub>6</sub> ·OH(β) .....	58.79
(m)NO <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> ·N <sub>2</sub> ·C <sub>10</sub> H <sub>6</sub> ·OH(β) ...	41.21 (by difference).

Calculated for equal molecules:—

(p)Br·C <sub>6</sub> H <sub>4</sub> ·N <sub>2</sub> ·C <sub>10</sub> H <sub>6</sub> ·OH(β) .....	52.74
(m)NO <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> ·N <sub>2</sub> ·C <sub>10</sub> H <sub>6</sub> ·OH(β) .....	47.26
	2 H 2

#### IV. THE TRIPLET FROM METANITRANILINE AND PARABROMANILINE CONTAINING ETHYL.

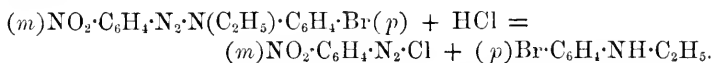
1. *Action of Diazotised Metanitriline on Ethylparabromaniline.*—Metanitriline was diazotised in the usual way, and the solution mixed with a solution containing the necessary quantity of ethylbromaniline hydrochloride. An ochreous viscid resin separated, and this on standing solidified to a brittle mass which was dissolved in alcohol and allowed to crystallise. After two crystallisations, the compound was obtained pure in the form of flat, ochreous bundles of needles nearly an inch in length and having a sharp melting point of 111°.

0.1054 gram gave 14.5 c.c. moist N at 10° C. and 744 mm. bar.

0.2201 „ 0.1171 gram AgBr.

	Calculated for ( <i>m</i> )NO <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub> ·N <sub>2</sub> ·N(C <sub>2</sub> H <sub>5</sub> )·C <sub>6</sub> H <sub>4</sub> ·Br( <i>p</i> ).	Found.
N .....	16.04	16.11
Br .....	22.92	22.64

*Decomposition by Hydrochloric Acid.*—0.3034 gram under 10 c.c. strong acid dissolved in three hours at the ordinary temperature, leaving 0.0125 gram residue, and gave 0.2354 gram azonaphthol, corresponding to 83.8 per cent. The azonaphthol was identified as pure metanitrobenzeneazo-β-naphthol (m. p. 194°), showing that the decomposition by acid takes place normally according to the equation—



The above equation requires a yield of 83.9 per cent. of metanitrobenzeneazo-β-naphthol, so that the resolution is strictly quantitative.

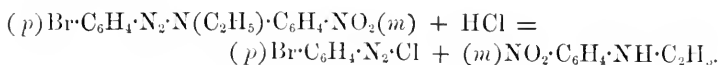
2. *Action of Diazotised Parabromaniline on Ethylmetanitriline.*—The solution of the diazo-chloride was mixed with the solution of ethylitriline in dilute hydrochloric acid and sodium acetate added to the mixture. An ochreous precipitate slowly separated, and after being allowed to stand in the cold for 18 hours this was collected, washed with water, and crystallised from alcohol. After three crystallisations, the pure substance was obtained in the form of glistening, yellow needles melting at 135—136°.

0.1605 gram gave 20.9 c.c. moist N at 8° C. and 764.4 mm. bar.

0.2231 „ 0.1207 gram AgBr.

	Calculated for	Found.
	$(p)\text{Br}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{N}(\text{C}_2\text{H}_5)\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2(m).$	
N .....	16.04	15.94
Br.....	22.92	23.02

*Decomposition by Hydrochloric Acid.*—0.3040 gram, under 10 c.c. of strong acid for 18 hours at the ordinary temperature, dissolved with the exception of 0.0016 gram, and gave 0.2804 gram azonaphthol, corresponding to 92.74 per cent. The latter had, when crude, a melting point of 168—171°, and was identified as parabromobenzeneazo- $\beta$ -naphthol. The decomposition therefore takes place normally, according to the equation—



According to the foregoing equation, the yield of azonaphthol should have been 93.7 per cent., so that the resolution by acid is practically quantitative.

3. *Ethylation of Metanitroparabromodiazamidobenzene.*—The substance used for ethylation was a portion of the same preparation as that employed for methylation, the process being carried out in the usual way with potassium hydroxide and ethyl iodide. After one crystallisation from alcohol, the substance was obtained in the form of microscopic ochreous needles melting at 96—117°.

0.1290 gram gave 17 c.c. moist N at 11.5° C. and 764.6 mm. bar.

0.1591           ,,           0.0860 gram AgBr.

	Calculated for	Found.
	$(m)\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_3(\text{C}_2\text{H}_5)\cdot\text{C}_6\text{H}_4\cdot\text{Br}(p).$	
N .....	16.04	15.78
Br.....	22.92	23.00

In order to test the individuality of this compound, it was again crystallised from a large volume of alcohol and the bromine determined. The melting point, so far as could be judged, considering its vagueness, had not materially altered:—

0.1587 gram gave 0.0850 gram AgBr.

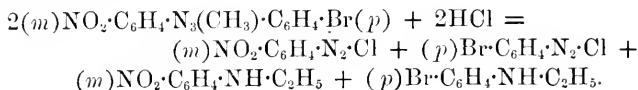
	Calculated.	Found.
Br .....	22.92	22.79

*Decomposition by Hydrochloric Acid.*—0.2899 gram under 10 c.c. strong acid dissolved at the ordinary temperature in 2—3 hours, with the exception of 0.0038 gram, and gave 0.2600 gram azonaphthol, corresponding to 90.87 per cent.

The azonaphthol when crude had a melting point  $145-155^{\circ}$  and, as usual, proved to be a mixture:—

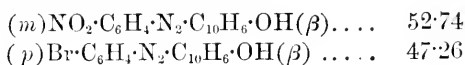
0.2234 gram gave 0.0792 gram AgBr = 15.08 per cent. Br.

The decomposition by acid, according to the following equation, requires a yield of 88.8 per cent. of mixed azonaphthols:—

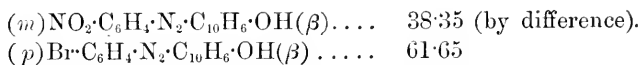


The mixed azonaphthols, if present in equal molecules, should contain 12.9 per cent. Br.

Calculated for equal molecules—



Found—



In this decomposition, it would appear therefore that an excess of parabromodiazobenzene chloride is produced. The significance of these quantitative decompositions will be discussed subsequently.

The compounds now described all contain the  $\text{NO}_2$  group in one of the aromatic nuclei, and our next experiments were directed towards the preparation of triplets of isomerides not containing this group. Our study of the dinitro- and nitro-bromodiazooamides revealed some general principles which have been made the basis of further work, and which have enabled us to achieve the long desired end of obtaining triplets of alkyl-derivatives not containing the group in question, and solid at ordinary temperatures (see Trans., 1888, 665). It will be seen from the foregoing results that the effect of introducing an alkyl radicle into a diazoamide is to lower the melting point, and in all the cases studied the methyl-derivative had a considerably higher melting point than the ethyl-derivative. These facts are shown in the accompanying table (p. 431), summarising our results with the nitranilines and bromaniline.

It will be seen from these results that in order to obtain alkyl-diazoamides solid at ordinary temperatures, it is in the first place essential to start from an unalkylated compound having a high melting point, and in the next place it is evident that the chances of the alkyl-derivative fulfilling the required conditions are greater the lower the molecular weight of the radicle introduced. It is the

Diazoamido-compound.	Unalkylated compound.	Methyl-derivative.	Ethyl-derivative.
I. From <i>p</i> -nitraniline and <i>p</i> -bromaniline .....	175—181	150·5—151·5°	115—116
II. Diazotised <i>p</i> -nitraniline on alkyl- <i>p</i> -bromaniline .....	—	151—151·5°	139—140
III. Diazotised <i>p</i> -bromaniline on alkyl- <i>p</i> -nitraniline .....	—	163—164°	124—125
I. From <i>m</i> -nitraniline and <i>p</i> -bromaniline.....	155 *	125—137·5°	96—117
II. Diazotised <i>m</i> -nitraniline on alkyl- <i>p</i> -bromaniline .....	—	144°	111
III. Diazotised <i>p</i> -bromaniline on alkyl- <i>m</i> -nitraniline .....	—	160·5—161°	135—136°

non-compliance with these conditions which has led previous experimenters to the preparation of alkyl-diazoamides which have been oily at ordinary temperatures, and which have therefore baffled close investigation. It will be of interest here to give one of our earlier attempts to prepare a triplet having the required properties.

The mixed diazoamide produced by acting with diazotised parachloraniline on paratoluidine, or *vice versa*, has a melting point of 129° (Heumann and Oeconomides, *Ber.*, 1887, 909), and therefore seemed a promising compound for our purpose. Some of the substance was prepared and ethylated, and the product found to be an oil which would not solidify. The oil was therefore decomposed by cold hydrochloric acid in the usual way, and the acid solution gradually poured into a well-cooled alkaline solution of  $\beta$ -naphthol. The azonaphthol precipitate was collected, washed with alkali, acid, and water successively, and dried. The melting point of the crude substance was 145—152°, and after four crystallisations from alcohol, pure parachlorobenzeneazo- $\beta$ -naphthol (m. p. 162·5°, *Trans.*, 1888, 676) was isolated from it. The oil was thus proved to be the ethyl-derivative (*p*)Cl·C<sub>6</sub>H<sub>4</sub>·N<sub>3</sub>(C<sub>2</sub>H<sub>5</sub>)·C<sub>6</sub>H<sub>4</sub>·CH<sub>3</sub>(*p*), and its products of decomposition the usual mixture of diazo-chlorides and bases. Another isomeride was then prepared by acting with diazotised paratoluidine on ethyl-parachloraniline, and this also proved to be an oil.

The introduction of ethyl into the diazoamide from parachloraniline

\* This is the melting point given by Goldschmidt for the substance crystallised from benzene (*Ber.*, 1888, 2575).

and paratoluidine therefore depresses the melting point to such an extent, that the product is oily at ordinary temperatures, and as two of the three isomerides were thus shown to be oils, the triplet was not further investigated. The corresponding series containing methyl will be described subsequently.

#### V. THE TRIPLET FROM PARABROMANILINE AND PARATOLUIDINE CONTAINING METHYL.

1. *Action of Diazotised Parabromaniline on Methylparatoluidine.\**—The secondary amine was employed in the form of the oxalate and the diazo-chloride solution mixed in as usual. On adding sodium acetate, an ochreous precipitate gradually separated, and after standing for about 24 hours this was collected, washed with cold water, and twice crystallised from alcohol. The pure substance forms small ochreous scales melting at 113–114°.

0.1853 gram gave 22 c.c. moist N at 15° C. and 760.3 mm. bar.

0.3056           ,,    0.1880 gram AgBr.

	Calculated for (p)Br·C <sub>6</sub> H <sub>4</sub> ·N <sub>2</sub> ·N(CH <sub>3</sub> )·C <sub>6</sub> H <sub>4</sub> ·CH <sub>3</sub> (p).	Found.
N .....	13.81	13.91
Br.....	26.31	26.18

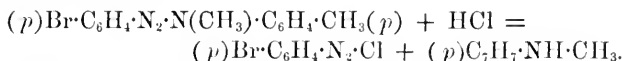
*Decomposition by Hydrochloric Acid.*—This compound is very readily decomposed by cold strong acid, dissolving completely in the course of a few minutes, and beginning to evolve nitrogen if allowed to stand long after it has completely dissolved. The quantitative results with strong acid always came out much too low, owing to the reaction going too far and the consequent formation of phenolic products. The decomposition of this and of the isomeric compounds was therefore effected by means of a mixture consisting of 5 parts (by volume) of strong acid diluted with 3 parts of water. 0.3258 gram in about 8 c.c. of dilute acid dissolved completely in about one hour and gave 0.3278 gram azonaphthol, corresponding to 100.6 per cent. The calculated yield is 107.5 per cent. The azonaphthol had when crude a melting point of 168°, which was not materially changed by crystallisation from alcohol, and was identified as parabromobenzeneazo-β-naphthol.

0.0844 gram crude substance gave 0.0478 gram AgBr.

	Calculated for Br·C <sub>6</sub> H <sub>4</sub> ·N <sub>2</sub> ·C <sub>10</sub> H <sub>6</sub> ·OH.	Found.
Br.....	24.46	24.10

\* We are indebted to Dr. A. Weinberg of the Frankfurter Anilinfarbenfabrik, Gans and Co., for kindly preparing a supply of the pure base for our investigation.

The decomposition accordingly takes place normally in accordance with the equation—



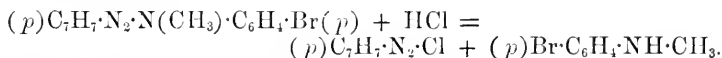
2. *Action of Diazotised Paratoluidine on Methylparabromaniline.*—The solution of paradiazotoluene chloride was mixed with the necessary quantity of methylparabromaniline oxalate dissolved in cold water, and sodium acetate dissolved in the mixed solutions. After being allowed to stand for 12 hours, the ochreous precipitate was collected, washed with cold water, and twice crystallised from alcohol. The pure substance forms splendid crystalline scales of considerable size, which glisten in the solution with prismatic colours. Under the microscope, the alcoholic solution when allowed to evaporate in a watch-glass is seen to deposit square transparent tablets. The appearance of the dry substance is very similar to that of sublimed naphthalene, only the crystals instead of being white are slightly ochreous in colour. The melting point is 99—99·5°.

0·2510 gram gave 30 c.c. moist N at 15° C. and 758·5 mm. bar.

0·1719           ,,       0·1072 gram AgBr.

	Calculated for ( <i>p</i> )C <sub>7</sub> H <sub>7</sub> ·N <sub>2</sub> ·N(CH <sub>3</sub> )·C <sub>6</sub> H <sub>4</sub> ·Br( <i>p</i> ).	Found.
N .....	13·81	13·94
Br.....	26·31	26·54

*Decomposition by Hydrochloric Acid.*—0·3202 gram dissolved completely in 8 c.c. dilute acid (5 : 3) in one hour at the ordinary temperature, and gave 0·2692 gram azonaphthol, corresponding to 84·1 per cent. The calculated yield is 86·2 per cent. The azonaphthol was tested for bromine, and found to contain none; the melting point of the crude substance was 132—133°, and after one crystallisation from alcohol 134°, that is, paratolueneazo-β-naphthol. The decomposition is therefore normal :—



3. *Methylation of Parabromobenzenediazoamidoparatoluene.*—The diazoamide was prepared by gradually mixing a solution of diazotised paratoluidine with the necessary quantity of parabromaniline emulsified in a solution of sodium acetate. After being allowed to stand for some hours, the ochreous precipitate was collected, washed with cold water, then with dilute alcohol, and allowed to dry in the air. During the course of our experiments, a description of this mixed diazoamide appeared from another investigator (Goldschmidt, *Ber.*,

1888, 2568, m. p., crystallised from benzene,  $126^{\circ}$ ), so the compound was not further studied, but was at once methylated in the usual way. The methyl-derivative, after three crystallisations from alcohol, the last with the addition of animal charcoal, was obtained in the form of large ochreous scales, exactly resembling the preceding isomeride in appearance, and melting at  $97-97.5^{\circ}$ .

0.2206 gram gave 25.4 c.c. moist N at  $13^{\circ}$  C. and 765 mm. bar.

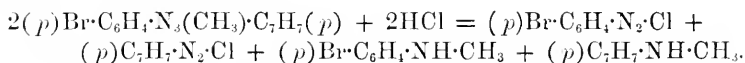
0.1560            „            0.0973 gram AgBr.

	Calculated for (p)Br·C <sub>6</sub> H <sub>4</sub> ·N <sub>3</sub> (CH <sub>3</sub> )·C <sub>7</sub> H <sub>7</sub> (p).	Found.
N .....	13.81	13.69
Br.....	26.31	26.54

*Decomposition of Hydrochloric Acid.*—The close resemblance, both in crystalline form and melting point, between this and the preceding modification, led us at first to believe that the two compounds were identical, and that the isomerism had in this case broken down. A study of the decomposition by hydrochloric acid, however, soon showed that the compounds, in spite of their similarity, were really isomeric. A specimen was decomposed by dilute acid in the usual way, and the azonaphthol submitted to a careful examination.

0.2558 gram gave 0.0783 gram AgBr = 13.62 per cent. Br.

The decomposition was not made quantitative in this case, owing to the small quantity of material at our disposal, but this is of no consequence to the present result. The azonaphthol was evidently a mixture melting when crude at  $138-150^{\circ}$ , and furnishing after three crystallisations from alcohol pure parabromobenzeneazo- $\beta$ -naphthol (m. p.  $168-170^{\circ}$ .) The decomposition of the methylated diazoamide accordingly takes place as follows:—



According to this equation, the azonaphthol should consist of molecular proportions of parabromobenzeneazo- $\beta$ -naphthol and paratolueneazo- $\beta$ -naphthol, this mixture containing 13.6 per cent. of Br (13.02 per cent. found), and having the following percentage composition:—

(p)Br·C <sub>6</sub> H <sub>4</sub> ·N <sub>2</sub> ·C <sub>10</sub> H <sub>6</sub> ·OH( $\beta$ ) .....	55.5
(p)CH <sub>3</sub> ·C <sub>6</sub> H <sub>4</sub> ·N <sub>2</sub> ·C <sub>10</sub> H <sub>6</sub> ·OH( $\beta$ ) .....	44.5

The percentage of bromine found corresponds to a mixture of the composition—

(p)Br·C <sub>6</sub> H <sub>4</sub> ·N <sub>2</sub> ·C <sub>10</sub> H <sub>6</sub> ·OH( $\beta$ ) .....	53.2
(p)CH <sub>3</sub> ·C <sub>6</sub> H <sub>4</sub> ·N <sub>2</sub> ·C <sub>10</sub> H <sub>6</sub> ·OH( $\beta$ ) ....	46.8 (by difference).



It is seen from this result that the decomposition fairly corresponds with the formation of equal molecules of the two diazo-chlorides as required by the equation. It is of particular interest also to note how easily the isomerism might have been overlooked in this case, unless we had been previously prepared to look for it by the investigation of the nitrobromodiazooamides.

*Paradibromodiazooamidobenzene and its Methyl-derivative.*

Amongst the normal diazoamides prepared in the course of the present investigation, the above, which was first described by Griess (*Annalen*, **121**, 273, and *Phil. Trans.*, 1864, Part III, 669), was methylated in order to obtain a supply of methylbromaniline, and the opportunity was utilised for the further study of this alkyl-derivative. The original compound was found to agree in all respects with that prepared by Griess. A specimen crystallised from a mixture of petroleum and benzene formed pale-yellow needles, melting with decomposition at 146°. It is insoluble in aqueous alkalis, but dissolves readily in alcoholic potash or soda, with a brown colour.

0·1670 gram gave 0·1774 gram AgBr.

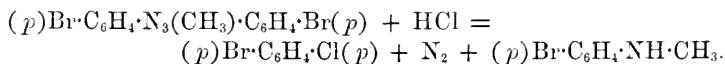
	Calculated for	
	( <i>p</i> )Br·C <sub>6</sub> H <sub>4</sub> ·N <sub>3</sub> H·C <sub>6</sub> H <sub>4</sub> ·Br( <i>p</i> ).	Found.
Br. ....	45·07	45·20

The methyl-derivative, prepared in the usual way, after crystallisation from alcohol and finally from a mixture of petroleum and benzene, forms flat, whitish needles, melting at 100—100·5°.

0·1482 gram gave 0·1512 gram AgBr.

	Calculated for	
	( <i>p</i> )Br·C <sub>6</sub> H <sub>4</sub> ·N <sub>3</sub> (CH <sub>3</sub> )·C <sub>6</sub> H <sub>4</sub> ·Br( <i>p</i> ).	Found.
Br. ....	43·36	43·41

The foregoing methyl-derivative was decomposed by heating with strong hydrochloric acid until nitrogen ceased to be given off. The acid liquor on dilution and distillation with a current of steam furnished a white, crystalline substance which, after crystallisation from alcohol, formed white scales melting at 67—68°, and therefore proved to be parachlorobromobenzene (Körner, *Gaz.*, **4** (1874), 342). The solution, after filtration to remove a resinous impurity, contained the required methylparabromaniline, so that the methyldiazoamide is decomposed by hot acid according to the equation—



## VI. THE TRIPLET FROM PARACHLORANILINE AND PARATOLUIDINE CONTAINING METHYL.

1. *Action of Diazotised Parachloraniline on Methylparatoluidine.*—The solution of the diazo-chloride was mixed with the solution of the oxalate of the secondary amine and sodium acetate added. An ochreous crystalline precipitate separated on standing, and this, after being collected, washed with water, and crystallised three or four times from alcohol, was obtained in the form of ochreous scales melting at 99·5–100°.

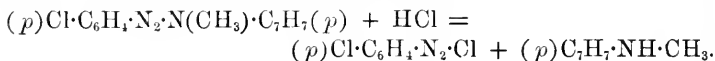
0·1387 gram gave 19·3 c.c. moist N at 15° C. and 764·4 mm. bar.

0·1569 „ 0·0886 gram AgCl.

	Calculated for (p)Cl·C <sub>6</sub> H <sub>4</sub> ·N <sub>2</sub> ·N(CH <sub>3</sub> )·C <sub>7</sub> H <sub>7</sub> (p).	Found.
N .....	16·19	16·39
Cl .....	13·68	13·96

*Decomposition by Hydrochloric Acid.*—0·3056 gram, allowed to stand for 10 minutes under 8 c.c. dilute acid (2 parts strong acid to 1 of water), dissolved completely at the ordinary temperature, and gave on precipitation 0·3250 gram azonaphthol.

The latter had, when crude, a melting point of 161°, and after one crystallisation from alcohol was identified as parachlorobenzeneazo-β-naphthol (m. p. 162·5°, Trans., 1888, 676). The quantity of azonaphthol obtained corresponds to 106·3 per cent. The decomposition therefore takes place normally, according to the equation—



The above equation requires a yield of 108·8 per cent. of parachlorobenzeneazo-β-naphthol.

2. *Action of Diazotised Paratoluidine on Methylparachloraniline.\**—On mixing the solutions in the usual way and adding excess of sodium acetate, an ochreous precipitate slowly separated. After being collected, washed, and crystallised two or three times from alcohol, the pure compound was obtained in the form of long straw-coloured needles melting at 91–92°.

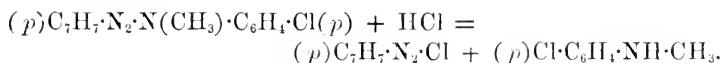
0·1110 gram gave 15·3 c.c. moist N at 14·5° C. and 758·4 mm. bar.

0·1254 „ 0·0705 gram AgCl.

\* Prepared by decomposing methylated *p*-dichlorodiazamidobenzene with hydrochloric acid. The methyl-diazoamide forms ochreous scales, melting at 74°. The corresponding ethyl-derivative melts at 85·5° (Trans., 1888, 671).

	Calculated for ( <i>p</i> )C <sub>7</sub> H <sub>7</sub> ·N <sub>2</sub> ·N(CH <sub>3</sub> )·C <sub>6</sub> H <sub>4</sub> ·Cl( <i>p</i> ).	Found.
N .....	16·19	16·13
Cl .....	13·68	13·88

*Decomposition by Hydrochloric Acid.*—0·3205 gram under 8 c.c. dilute acid (2 parts strong acid to 1 of water) dissolved completely in 10 minutes, and gave on precipitation 0·3170 gram azonaphthol, corresponding to 98·9 per cent. The latter had, when crude, a melting point of 133°, and after crystallisation from alcohol was identified as paratolueneazo-β-naphthol (m. p. 134·5°). The decomposition is therefore normal :—



According to this equation, the yield of paratolueneazo-β-naphthol should have been 100·96 per cent.

3. *Methylation of Parachlorobenzendiazoamidoparatoluene.*—The usual difficulties were experienced, and several preparations of the mixed diazoamide were made before a perfectly pure methyl-derivative was obtained. Good results were given by a preparation made by pouring a solution of diazotised parachloraniline (1 mol.) into an alcoholic solution of paratoluidine (2 mols.). The product, which separates as an ochreous crystalline deposit, was collected, drained, and dried, and then at once methylated by heating gently with potassium hydroxide and methyl iodide in alcoholic solution in the usual way. Methylation takes place very readily if the solution is concentrated, the contents of the flask solidifying in a few minutes to a crystalline pulp. The product, after being collected and washed with water, was purified by two or three crystallisations from alcohol, and then formed large ochreous scales melting at 80—82°.

0·1397 gram gave 19·3 c.c. moist N at 13·5° and 758·2 mm. bar.

0·2008           ,,           0·1093 gram AgCl.

	Calculated for ( <i>p</i> )Cl·C <sub>6</sub> H <sub>4</sub> ·N <sub>3</sub> (CH <sub>3</sub> )·C <sub>7</sub> H <sub>7</sub> ( <i>p</i> ).	Found.
N .....	16·19	16·24
Cl .....	13·68	13·47

Another preparation was made by reversing the order of mixing. Paratoluidine was diazotised in the usual way, and a small excess of the base added in order to ensure the absence of any trace of free nitrous acid. The solution of the diazo-chloride was then gradually poured with constant stirring into the necessary quantity of parachloraniline suspended as an emulsion in a solution of sodium acetate.

After being allowed to stand for some hours in the cold, the product was collected, washed, drained, and dried, and methylated in the usual way. The methyl-derivative after two crystallisations from alcohol proved to be quite pure and was identical in all respects with the preceding preparation, thus furnishing another instance in support of Griess's discovery that mixed diazoamides are identical in whichever order the two amines are diazotised and combined. The analysis of this preparation is given below:—

0.1270 gram gave 18.4 c.c. moist N at 20.5° and 760 mm. bar.

0.1695       .,       0.0928 gram AgCl.

	Calculated.	Found.
N .....	16.19	16.43
Cl.....	13.68	13.54

*Decomposition by Hydrochloric Acid.*—0.2983 gram in 10 c.c. dilute acid (2 of strong acid to 1 of water) dissolved completely in 15 minutes, and gave on precipitation 0.320 gram azonaphthol, corresponding to 107.3 per cent. Theory (for molecular proportions) requires 104.9 per cent. The azonaphthol proved as usual to be a mixture having in the crude state a melting point 135—145°.

0.2666 gram gave 0.0787 gram AgCl = 7.30 per cent. Cl.

The amount of chlorine found corresponds to a mixture of the following percentage composition:—

$(p)\text{Cl}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}(\beta)$ .....	58.09
$(p)\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}(\beta)$ ....	41.91 (by difference).

Calculated for equal molecules the results are:—

$(p)\text{Cl}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}(\beta)$ .....	51.88
$(p)\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}(\beta)$ ....	48.12

A mixture of the above composition contains 6.52 per cent. of Cl.

*Discussion of the Results obtained by the Method of Quantitative Decomposition.*

By the action of hydrochloric acid on the diazoamides, these compounds are decomposed in the first place with the formation of the diazo-chloride and the amine or alkylamine, in accordance with the reactions given in the preceding portion of the paper. The quantitative results obtained by weighing the washed and dried azonaphthol compound, are on the whole sufficiently close approximations to the numbers indicated by theory to warrant the conclusion that the molecules break up in the manner indicated. In the case of the mixed

diazoamides, however, which, in all the cases investigated, give a mixture of two diazo-chlorides and two amines, it is obviously a matter of great importance to ascertain the relative quantities of the two diazo-chlorides with the greatest possible accuracy, in order to settle the question whether one molecule of the mixed diazoamide breaks up exactly into the 4 mols., as represented in the equation—



The actual results deduced from the analyses of the mixed azo-naphthols show, in nearly all cases, a slight excess of halogen over that required by equimolecular proportions of the two azonaphthols, as will be seen most clearly from the tabulated results:—

Compound decomposed.	Halogen p. e. calculated for.	Halogen found.
$(p)NO_2 \cdot C_6H_4 \cdot N_3(CH_3) \cdot C_6H_4 \cdot Br(p) \dots$	$(p)NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot OH(\beta) +$ $(p)Br \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot OH(\beta)$ Br = 12.9	15.56
$(p)NO_2 \cdot C_6H_4 \cdot N_3(C_2H_5) \cdot C_6H_4 \cdot Br(p) \dots$	$(p)NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot OH(\beta) +$ $(p)Br \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot OH(\beta)$ Br = 12.9	14.83
$(m)NO_2 \cdot C_6H_4 \cdot N_3(CH_3) \cdot C_6H_4 \cdot Br(p) \dots$	$(m)NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot OH(\beta) +$ $(p)Br \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot OH(\beta)$ Br = 12.9	14.38
$(m)NO_2 \cdot C_6H_4 \cdot N_3(C_2H_5) \cdot C_6H_4 \cdot Br(p) \dots$	$(m)NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot OH(\beta) +$ $(p)Br \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot OH(\beta)$ Br = 12.9	15.08
$(p)Br \cdot C_6H_4 \cdot N_3(CH_3) \cdot C_6H_4 \cdot CH_3(p) \dots$	$(p)Br \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot OH(\beta) +$ $(p)CH_3 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot OH(\beta)$ Br = 13.6	13.02
$(p)Cl \cdot C_6H_4 \cdot N_3(CH_3) \cdot C_6H_4 \cdot CH_3(p) \dots$	$(p)Cl \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot OH(\beta) +$ $(p)CH_3 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot OH(\beta)$ Cl = 6.52	7.30

Considering that the method of determining the relative quantities of the different products of decomposition is necessarily only approximative, we consider these numbers sufficiently close to those required by theory to warrant the conclusion that the decomposition results in the formation of the two diazo-chlorides in molecular proportion. The error being (with one exception) always on the side of excess of halogen, it is evident, however, that for some reason, an excess of the halogen-containing diazo-salt tends to be produced, the haloid azo- $\beta$ -naphthol coming out correspondingly high. We thought it

desirable at this stage of the work, therefore, to investigate the quantitative method itself, with the object of ascertaining whether the excess of halogen arose from the occurrence of some secondary reaction, a supposition which seemed highly probable in view of the well-known instability of the diazo-salts in solution. Taking the first of the mixed diazoamides in the table as a typical compound, it will be seen that the four products existing in the acid solution after the decomposition are—



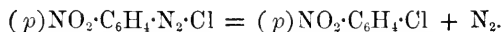
The best known secondary decompositions which might occur in such a mixture are the following:—

(1.) Paranitrodiazobenzene chloride might become transformed into the corresponding nitrophenol, according to the well-known decomposition:—



The nitrophenol would dissolve in the alkaline solution of  $\beta$ -naphthol, and would thus be lost, giving at the same time a product containing an excess of bromazo- $\beta$ -naphthol, thus raising the percentage of bromine. Against this interpretation of the facts we may state that we have never been able to detect any nitrophenol in the alkaline filtrate, nor have we ever observed any evolution of nitrogen. It will be seen, moreover, that if any nitrophenol were formed there would be a deficiency in the total weight of the mixed azonaphthols, whereas we actually found an excess (calculated percentage 92.5; found 95).

(2.) Paranitrochlorobenzene might be formed in accordance with the mode of decomposition described by us in a former paper (Trans., 1886, 629)—



This nitrochlorobenzene being neither acid nor basic, might cling to the azonaphthols, and so raise the percentage of halogen. In order to see whether this explained the presence of the excess of halogen, the following experiment was made:—1 gram of paranitraniline was diazotised in strong hydrochloric acid with a slight excess of sodium nitrite, and the solution allowed to stand at the ordinary temperature for about 18 hours. The solution was diluted with water, and filtered through a tared filter into an alkaline solution of  $\beta$ -naphthol. The residue on the filter, when dry, weighed 0.0038 gram. The azonaphthol precipitate was collected, washed with water, then with dilute acid, and again with water, in precisely the same way as when doing a

quantitative decomposition by our method. The dry precipitate weighed 2·0644 grams, corresponding to 207·2 per cent. The theoretical yield should have been 212·3 per cent. A chlorine determination in the dried azonaphthol gave the following results:—

1·1571 gram gave 0·0048 gram AgCl = 0·10 per cent. Cl.

We conclude from this experiment that the amount of chlorine retained by the azonaphthol is far too small to account for the excess of halogen obtained in the quantitative decomposition of the nitrobromo-diazoamides.

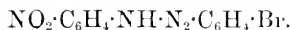
The two most feasible explanations having thus proved to be insufficient, we had recourse to an experiment in which the compounds reacting in the acid solution were similar to those which might be supposed to react during the process of quantitative decomposition. For this purpose, we took 0·9661 gram of the compound produced by the action of diazotised metanitraniline on methylparabromaniline, described in a former part of this paper, and allowed 15 c.c. of strong hydrochloric acid to act upon this quantity for about 48 hours, the beaker being kept cool by standing it in water. The operation was then completed in the usual way, and the dried azonaphthol examined for bromine:—

0·1878 gram gave 0·0199 gram AgBr = 4·5 per cent. Br.

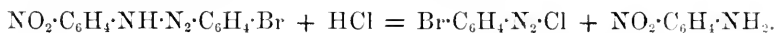
If the decomposition had been arrested at the usual stage, that is, as soon as the substance had completely dissolved up in the acid, the azonaphthol should have been simply metanitrobenzeneazo- $\beta$ -naphthol, and should have contained no bromine. The presence of bromine appears, therefore, to indicate that some secondary reaction occurs, leading to the formation of bromobenzenediazo-chloride, and of the corresponding bromobenzeneazonaphthol. The most probable explanation which we can suggest is that the nitrodiazo-chloride causes a certain amount of displacement of the methyl-group:—



The mixed diazoamide then becoming converted by intramolecular transposition into the isomeric and more stable compound—

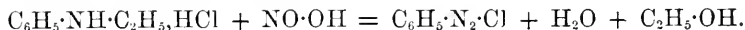


The latter again becoming resolved by acid—



Such a secondary reaction as this would of course go on concurrently with the primary resolution, the amount of bromobenzene-

diazo-chloride formed increasing with the time. We are disposed to believe that this is the true explanation of the excess of halogen found in the cases under discussion, and that the normal decomposition of the mixed alkyl-diazoamide results in the production of the two diazo-chlorides in *equal* molecular proportions. A small quantity of bromine or chlorine in excess of that required by equal molecular proportions of the two diazo-chlorides would obviously become exaggerated if calculated as chloro- or bromo-benzeneazo- $\beta$ -naphthol. Thus the 4.5 per cent. of bromine found after 48 hours' action of the acid corresponds to over 18 per cent. of the bromazonaphthol, so that a very small amount of secondary decomposition would suffice to raise the percentage of the bromazonaphthol to the extent found in our analyses. We may here point out that the action of the nitrodiazo-chlorides upon secondary alkylamines seems worthy of special investigation from this point of view. That the secondary reaction is of the nature indicated is rendered probable by an observation due, originally, to Griess (*Phil. Trans.*, Part III, 1864, 694), and since repeated in all the text-books. According to this observation, nitrous acid is capable of expelling ethyl from ethylaniline with the formation of the diazo-salt:—



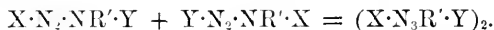
If nitrous acid can react in the way stated, it is not improbable that a diazo-salt of a radicle containing a strongly acid group ( $\text{NO}_2$ ), may act in an analogous manner.

#### *Summary and Conclusion.*

1. The six triplets of mixed alkyl-diazoamides described in the present paper, together with the two cases made known in former communications, suffice to establish the reality of the isomerism first made known by us in 1887 (*Trans.*, **51**, 443).

2. The decomposition of the alkyl-derivatives of mixed diazoamides by cold hydrochloric acid into a mixture containing equal molecular proportions of two diazo-chlorides, suggests that the molecular weight of these compounds is double that usually assigned.

3. In support of this conclusion we have recently found that mixed alkyl-diazoamides, apparently identical with those produced by direct alkylation, can be formed synthetically by simply boiling together solutions of the other two members of the triplet, according to the equation—



This discovery forms the starting point of a new research, which has already been commenced in our laboratory, and which will, we



anticipate, lead to the final solution of the vexed question of the constitution of the diazoamido-compounds. We propose to determine the molecular weights of the isomerides by Raoult's method, using benzene as a solvent. In the meantime the chemical evidence appears to us to point to the conclusion that the *mixed* diazoamides, at any rate, are formed by the coalescence of two isomeric molecules, and that they accordingly contain the closed chain of nitrogen-atoms:—



It gives us great pleasure, in conclusion, to acknowledge the great assistance which we have received in conducting the necessarily laborious series of experiments required by the present research from two of our students, Messrs. G. T. Morgan and J. H. Coste, who have been good enough to prepare many of the products, and to make most of the analyses given in the paper. We desire also to acknowledge valuable contributions of preparations made for us by the Frankfurter Anilinfarbenfabrik, Gans and Co. The present work has been partly carried on by the aid of a grant from the Government Grant Fund of the Royal Society.

*Finsbury Technical College,*  
*June, 1889.*

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### XLIII.—On the Atomic Weight of Zinc.

By J. H. GLADSTONE, Ph.D., F.R.S., and WALTER HIBBERT, F.I.C.

WHILST using a zinc voltameter, recently arranged by one of us, Mr. Hibbert, it was observed that the loss in weight of the anode was very constant. The zinc deposited on the cathode was either not pure, or else it oxidised during washing, so that we could get no sufficient regularity in the results from it. The constancy in the loss of weight at the anode, which at first was somewhat surprising, inasmuch as the zinc was far from pure, seemed reasonable enough when considered in the light of the electrochemical position of zinc as compared with its ordinary impurities. These are all electronegative to zinc, and therefore are easily displaced in their compounds by that metal. If therefore during the action which takes place at the anode, any of the impurities should be taken up by the acid constituent of

the electrolyte, they ought immediately to be displaced by the more electropositive zinc. Some explanation of this sort seems needed to account for the result of our experiments. It was confirmed by occasional analysis of the liquid and the deposited zinc, these being found free from cadmium, lead, tin, and arsenic, and showing only minute traces of iron.

It then naturally occurred to us that it would be possible to get a fair estimate of the atomic weight of zinc by means of Faraday's electrolytic law.

Reynolds and Ramsay (Trans., 1887, 854) have given a considerably higher value for this number than most of the other experimenters. They determined the hydrogen liberated from acids by a known weight of zinc, the metal having been carefully prepared by precipitation as zinc sulphide, re-solution as sulphate and subsequent electrolytic deposition, with final fusion in an exhausted hard glass tube. The mean result gave the atomic weight as 65·478, and the authors think it quite possible that the true value may be 65·5. Previous values given in recent years are—

Marignac .....	65·180
Baubigny .....	65·184
Van de Plaats .....	65·180

These are reckoned for  $O = 15·963$ , and are taken from the paper by Reynolds and Ramsay already alluded to. Since that paper was written, another determination has been made by Morse and Burton (*Amer. Chem. J.*, 10, 311—321). They estimated the zinc oxide obtained from known weights of zinc, the metal having been obtained by a special kind of fractional distillation in a vacuum. The mean result gave the atomic weight as 65·106. This figure is very nearly the same as the three given above, but differs materially from the value given by Reynolds and Ramsay. The methods which yield these varying values involve either laborious operations to get pure zinc, or some dependence on the purity and stability of various compounds.

Our experiments, already alluded to, seemed to relieve us from the necessity of attempting to procure pure zinc, and gave promise of a result by the simplest operations. The values we give below are divided into two sets, the one obtained by determining the ratio between the equivalents of silver and zinc, the other depending on the ratio of zinc to copper. The first of these two ratios is likely to give a more accurate value for the atomic weight, seeing that the silver voltameter is a more accurate instrument than the copper one, and also that the atomic weight of silver is more accurately known than that of copper.

In all the experiments given, the circuit consisted of—

- (a.) A battery of four cells. These were modified Grove's cells, the sulphuric acid being replaced by sodium sulphate.
- (b.) A tangent galvanometer to indicate roughly the value of the current, and enable us to see that it was reasonably constant.
- (c.) A silver voltameter.
- (d.) A copper voltameter.
- (e.) Two zinc voltameters.

In one of the experiments the copper receiving plate was injured, so that it is omitted.

In the copper and silver voltameters, the conditions were similar to those shown to be best by the researches of Lord Rayleigh, Gray, and others.

The silver voltameter consisted of a platinum dish, 3 inches in diameter, as cathode, and a bundle of thick silver wires as anode. The latter were wrapped round with fine muslin and filter-paper to prevent particles falling into the dish below. The silver nitrate solution always contained about 15 per cent. of the salt. At the end of an experiment, the solution was poured from the platinum dish, and the latter then placed in a large vessel containing distilled water, which was slowly heated to about  $80^{\circ}$ . After decanting off, fresh water was poured into the vessel, and the operation repeated until the water showed no trace of silver. The platinum dish was then dried over a bunsen flame, adequately protected from the direct play of the heated gases.

The copper voltameter consisted of two copper plates and a slightly acid solution of copper sulphate, of sp. gr. about 1.75. After each experiment the copper receiving plate was rapidly washed with water, then with alcohol, and dried at a temperature of about  $40^{\circ}$ .

In each of the two zinc voltameters we used *amalgamated* sheet zinc as anode. Only one side of this was used, and we found it advantageous to fix it horizontally at the top of the liquid, so that only the under surface and edges were acted on. Experience showed that if the disc were fixed vertically, the distribution of mercury is altered as the action proceeds. It accumulates at the bottom of the zinc plate, leaving a poorer amalgam in the higher parts, and thereby introduces a possible source of error. In one or two cases the zinc was amalgamated by dipping the metal in a solution of mercuric nitrate, but the following method was preferred:—One side of the disc was rubbed with dilute sulphuric acid, and while still wet a large drop of mercury was allowed to fall on the centre. This was then rubbed over the whole surface, and allowed to stand, with occasional rubbing, till the amalgam had set. After thus setting, the

plate was well washed and dried. A copper wire was now soldered to the centre of the unamalgamated side, to be used both as a support and as a conductor for the current.

The anode thus prepared was treated in the same way before and after an experiment, that is to say, it was well washed in water, then in 0·805 alcohol, and dried at about 40°. We did not go beyond this, because we had in one or two experiments found slight traces of oxidation at higher temperatures.

The cathode was in most cases a copper dish containing the liquid, but in those instances where it was intended to test the liquid or deposited zinc, we used a platinum wire lying underneath the anode. The electrolyte was a solution of zinc sulphate, the sp. gr. of which varied from 1·18 to 1·21.

The following tables include all the experiments, excepting only those which were preliminary. The density of current as given in the third column, is expressed in ampères per square centimetre of the zinc anode.

Comparison of silver and zinc.					Ratio $\frac{\text{Ag.}}{\text{Zn}}$
No. of expt.	Duration.	Density of current.	Zinc dissolved.	Silver deposited.	
	mins.		grams.	grams.	
I .....	75	0·073	0·7767	2·5589	3·2945
" .....	"	0·159	0·7758	"	3·2984
II .....	72	0·120	0·5927	1·9551	3·2986
" .....	"	0·060	0·5924	"	3·3003
III .....	50	0·070	0·2277	0·7517	3·2969
" .....	"	0·033	0·2281	"	3·2955
IV .....	60	0·200	0·7452	2·4588	3·2995
" .....	"	0·090	0·7475	"	*3·2894
V .....	80	0·170	0·8770	2·9000	†3·3067
" .....	"	0·090	0·8784	"	3·3015
VI .....	75	0·044	0·9341	3·0809	3·2982
" .....	"	0·022	0·9347	"	3·2961
				Mean .....	3·2980

As far as the zinc voltameter is concerned, there are two chief sources of error in the above experiments. First, the possibility of small particles of the anode becoming loose and falling away. Secondly, the possibility of oxidation taking place during the washing and drying of the zinc sheet.

We have some slight reason to suspect that the result marked \*, is affected by the first of these sources of error. The zinc had been used in each of the previous experiments, and on examination its

edges were found to be thin, so that it had to be rejected for the subsequent experiments.

The result marked † is also a little doubtful. After washing, the surface of the zinc was found to be darker and duller than usual. It strongly suggested surface oxidation, but we could not test the point. We might have been justified in leaving these two results out, but we prefer to show the extreme differences obtained by the method.

The general regularity of the other results leads us to think there was little or no disturbance from the two sources of error named. Experiment showed that the second was ordinarily inoperative. We tried several times to see if repeated washing and drying had any influence on the weight of the zinc, but got only minute changes which would not affect the ratio.

It may be useful here to say that the first five experiments (involving 10 ratios) were made with special redistilled zinc obtained from Hopkin and Williams. The last experiment giving the two ratios 3.2982 and 3.2961 was made with two sheets cut from a piece of common zinc, bought at the nearest zinc-workers. It will be noticed that the two ratios with this zinc agree very well, although the current density is twice as great in one case as in the other.

The mean ratio of the equivalents of silver and zinc, as given by our experiments, is  $3.298 \pm 0.0008$ . If we take 107.93 as the atomic weight of silver, and the atomicity of zinc as 2, the atomic weight of zinc is—

$$\frac{107.93 \times 2}{3.2980} = 65.44.$$

If, as seems preferable, silver be taken as 107.66, then zinc is—

$$\frac{107.66 \times 2}{3.298} = 65.29.$$

We give below the comparison between zinc and copper. The density of current for the copper receiving plate varied comparatively little from 1 ampère per 50 square centimetres of receiving surface, the lowest density being 1 ampère for 70 square centimetres. It is known that the solution of copper sulphate acts on copper, but when slightly acid, and with these densities of current, the solvent action is small. Still the ratio obtained is not so reliable as that given by the preceding table for silver. As a matter of fact, the copper voltameter had only been used in the early experiments to give a ready check on the others. The ratios between silver and copper, which vary between 3.400 and 3.408, indicated a very fairly good agreement with the already known value, and afforded strong presumption that the ratio Zn : Cu would be sufficiently useful as a confirmation of the other results.

No. of expt.	Duration.	Zinc dissolved.	Copper deposited.	Ratio $\frac{\text{Zn}}{\text{Cu}}$ .
I .....	75 minutes	0.7767	0.7526	1.0313
" .....	"	0.7758	"	1.0308
II .....	72 minutes	0.5927	0.5737	1.0331
" .....	"	0.5924	"	1.0326
III .....	50 minutes	0.2277	0.2209	1.0308
" .....	"	0.2281	"	1.0326
V .....	80 minutes	0.8770	0.8510	1.0305
" .....	"	0.8784	"	1.0322
VI .....	75 minutes	0.9341	0.9038	1.0306
" .....	"	0.9347	"	1.0342
			Mean .....	1.0322

The mean ratio for Zn : Cu is, therefore, 1.0322. As the solvent action of the solution, already alluded to, is likely to give figures for copper a trifle lower than they ought to be, the ratio will be affected in an inverse sense—that is, the figure 1.0322 is very probably a trifle too high.

The values given for the atomic weight of copper vary somewhat. Three determinations made in recent years agree fairly well in giving a higher value than that formerly accepted. W. N. Shaw, as the result of many electrolytic experiments (*B. A. Report*, 1886) and a careful discussion, suggests 63.33.

T. W. Richards (*Amer. Chem. J.*, **10**, 187—191) has used a simple and apparently accurate method, namely, the precipitation of silver from a solution of its nitrate by known weights of copper. The mean result was 63.43.

Baubigny has given a value very nearly the same as Shaw's, and, as the latter was obtained by a method like that followed by us, we use it for our calculation. From it we get—

$$63.33 \times 1.0322 = 65.37,$$

as the atomic weight of zinc.

But this number (65.37) is obtained by means of a ratio which we have already seen to be too high, probably by something like one part in a thousand.

Reviewing the whole of the results, and attaching greater weight to the value derived from silver, the atomic weight of zinc would appear to be very close to 65.3. This is slightly higher than the figures given by Marignac, Baubigny, Morse and Burton, but somewhat lower than the value given by Reynolds and Ramsay.

# XLIV. *The Amylodextrin of W. Nägeli, and its relation to Soluble Starch.*

By HORACE T. BROWN, F.R.S., and G. HARRIS MORRIS, Ph.D., F.I.C.

IN the year 1874, W. Nägeli described, under the name of amylo-dextrin (*Beiträge zur Kenntniss der Stärkegruppe*, Leipzig), a substance which he obtained by the long-continued action of dilute mineral acids upon ungelatinised starch in the cold. The starch-granules, whilst retaining for some considerable time their original structure, were, in the course of several weeks, completely disintegrated, a portion of their substance going into solution in the acid, whilst the iodine reaction of the insoluble residue gradually changed from blue through violet to reddish-yellow. The residue consisted of crude amylo-dextrin, which was purified by solution in hot water and subsequent precipitation, either by freezing the solution, or by the addition of alcohol.

Nägeli describes amylo-dextrin as separating from its solutions in the form of crystalline spherules which are made up of minute needles arranged radially. The drawings which he gives of these crystalline aggregates suggest a close resemblance to the well-known spherules of *inulin*.

Amylo-dextrin is said to have a rotatory power of  $[\alpha] = 175^\circ$  to  $177^\circ$  when observed in the Wild's instrument with ordinary light; and it is also stated to be non-diffusible.

Of late years, the few chemists who have noticed amylo-dextrin have taken it for granted that it is identical with *soluble starch*, an opinion for which Musculus and Gruber (*Bull. Soc. Chim.*, **30**, 54, 1878) and Arthur Meyer (*Botan. Zeitung*, 1886, Nos. 41 and 42) are mainly responsible; whilst Tollens also adopts this view in his recent *Handbuch der Kohlenhydrate*.

A careful investigation of this little-known substance has, however, convinced us that it is a perfectly well-defined compound and entirely different in its nature from soluble starch. We are now in a position to define its properties more accurately, and to assign it a place in the series of starch-transformation products.

In describing his method for the determination of diastatic power, C. Lintner has stated (*J. pr. Chem.*, **34**, 378, 1886) that a comparatively short treatment of ungelatinised potato-starch with hydrochloric acid of 7.5 per cent. renders the granules, when subsequently freed from acid, capable of completely dissolving in hot water without the production of the usual viscid paste. Our experiments fully confirm

the accuracy of this statement. In one case in which the above-mentioned strength of acid had been used, the starch had lost all power of gelatinisation within 10 days; whilst in another experiment, in which acid of 12 per cent. had been used, this point was reached in less than 24 hours.

This extraordinary change in the properties of the granules is not accompanied by the slightest change of structure, and the altered granules have exactly the same influence on polarised light as the unaltered starch.

We have very carefully examined the nature of the substance which goes into solution on treatment of the altered starch with hot water, and find that it is in every way identical with the *soluble starch* described by O'Sullivan and others, and prepared by the limited action of heated malt-extract or of acid upon *starch-paste* heated to a suitable temperature.

Soluble starch prepared by any of these methods slowly separates out on long standing of its concentrated solutions, or immediately on the addition of alcohol to dilute solutions, as a white substance which in mass is somewhat pasty in its nature, and on washing with alcohol and subsequent drying becomes very friable. No matter how slowly it may be precipitated from its solutions, it is always found under the microscope to be made up of minute particles *entirely without structure* and without action on polarised light. The substance itself and also its solutions are coloured an intense blue by iodine. Although almost insoluble in cold water, it is readily soluble in water at 60–70°, and is thrown down again on cooling as a white, flocculent, amorphous precipitate.

The specific rotatory power of soluble starch in solution is  $[\alpha]_{D^{20}} = 216.0^\circ$ , and it has no cupric reducing power.

We have shown in our previous papers that soluble starch, which is the first product of the action of diastase on starch-paste, is capable, at temperatures up to 60°, of rapid hydrolysis down to a certain definite point, beyond which progress is relatively very slow. This point of equilibrium is reached before the complete transformation of the starch into maltose, the reaction becoming almost stationary when the mixed products give the following numbers:—

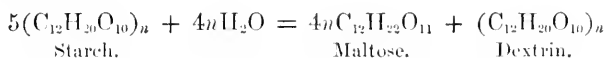
$[\alpha]_{D^{20}}$ .....	162.6°
$\kappa_{D^{20}}$ .....	49.3

corresponding to a composition of—

Maltose.....	80.9
Dextrin .....	19.1
	<hr/>
	100.00



and to the equation—



In the above-mentioned properties, the soluble starch prepared by the limited action of diastase or acids upon starch-paste, agrees in every particular with the soluble starch produced by the action of dilute acid upon starch-granules in the cold. This will be seen more clearly when we describe the gradual changes which take place in the granules during the last-mentioned process.

Before considering the chemical changes which occur during the continued digestion of starch with dilute acid, it will be well to point out the successive changes in appearance which the granules exhibit under the microscope.

When we employ 12 per cent. hydrochloric acid, it is not until about the twentieth day that any visible action is apparent, the first signs of disintegration of the granules being afforded by their splitting in a direction parallel with their shortest perimeter. Subsequently radial clefts are formed, and at the end of about two months the granules have become more or less disintegrated, especially in the direction of their stratification, this disintegration being complete in from three to four months, when the residual substance retains little or nothing of the original form of the starch-grain.

Concurrently with the changes mentioned above, the iodine reaction of the residual starch undergoes considerable modification, even before any change can be detected in the structure of the granule. The original pure blue colour given by iodine gradually changes through purple, reddish-purple and reddish-brown, to a pale yellowish-red, which is not further modified even if the starch remain in contact with the acid for some years.

The residual substance, after prolonged action of acid, is the crude amyloextrin of W. Nägeli and A. Meyer. This, as will be seen from our subsequent experiments, has been derived from the soluble starch first formed, by a gradual process of hydrolysis.

The time required to reach the final result has been stated by other observers to be about 100 days, but our own experiments point to this period as being insufficient for obtaining the maximum effect.

The final product which we will first describe had been in contact with the dilute acid for eight years and a half, the insoluble residue representing about 60 per cent. of the potato-starch originally taken. The residue under the microscope appeared to be made up of the disintegrated lamellæ of the original starch-granules, and was found to be coloured a light yellowish-red by iodine, and to be almost completely soluble in hot water. It was purified from the small quantity

of foreign matter it contained by precipitation from its aqueous solution by alcohol, or by immersing its solution in a freezing mixture. It is thrown down in the form of a brilliant white powder, which is highly crystalline in appearance when the precipitation has taken place slowly. Under the microscope, the precipitate is seen to consist of *sphæro-crystals* made up of thin needles or plates arranged radially, and so closely resembling the sphæro-crystals of inulin that the two substances cannot be distinguished by microscopical examination alone.

W. Nägeli (*loc. cit.*) gives very good illustrations of these crystalline aggregates, and also shows their appearance when viewed in polarised light.

Amylodextrin in solution gives with iodine an intense reddish-brown coloration.

The crude product on solution in water gave the following numbers, the amount of substance per 100 c.c. of the solution being 4.147 grams:—

$[\alpha]_{j3.86}^*$ .....	207.7°
$\kappa_{2.86}$ .....	9.09

After careful purification by precipitation with alcohol, the crystalline amyloidextrin gave the following constants:—

*Solution Density.*—A solution containing per 100 c.c. 5.8036 grams of amyloidextrin dried at 100° had a sp. gr. at 20° of 1022.701 (water at 20° = 1000), hence the divisor to be applied to solutions of this degree of concentration is 3.9115.

*Specific Rotatory Power.*—(1). A solution containing 5.8811 grams per 100 c.c. (3.86 divisor) gave in the Soleil-Ventzke-Scheibler instrument a reading of 63.0 scale divisions when observed in the 200 mm. tube.

(2.) In another case, a solution containing 6.4974 grams per 100 c.c. gave a reading under the same conditions of 70.1 divisions. These correspond to a specific rotatory power of—

(1.) $[\alpha]_{j3.86}$ .....	205.7°
(2.) $[\alpha]_{j3.86}$ .....	206.8
Mean $[\alpha]_{j3.86}$ .....	206.25°

*Cupric-reducing Power.*—10 c.c. of solution (1) used in the determination of the specific rotatory power, gave 0.1171 gram CuO; a second determination of the same solution gave 0.1176 gram CuO.

Solution (2)—10 c.c. gave 0.1306 gram CuO.

\* The values for the specific rotatory power  $[\alpha]_j$ , and for the cupric-reducing  $\kappa$ , are calculated throughout upon the 3.86 divisor for the total solids, and are in accord with the results given in our previous papers.

These results correspond to a cupric-reducing power of —

(1) <i>a.</i>	$\kappa_{3.86}$	9.04
(1) <i>b.</i>	$\kappa_{2.86}$	9.07
(2).	$\kappa_{3.86}$	9.12
	Mean $\kappa_{3.86}$	9.07.

The values of  $[\alpha]_j$  and  $\kappa$  deduced from the *actual weight* of amylo-dextrin employed are—

$[\alpha]_j$	208.42
$\kappa$	8.93

The apparent percentage composition of amylo-dextrin deduced from the mean values given above for the 3.86 divisor is\*—

Maltose	....	14.87	} which re-	{	$[\alpha]_{j3.86}$	....	205.4°
Dextrin	....	85.13			quires	$\kappa_{3.86}$	.....
<hr/>							
100.000							

We have now to consider if amylo-dextrin is a mixture of two or more substances, or if it is to be regarded as a homogeneous substance of definite chemical composition. In the first place it will be noticed that, however we regard it, the analytical numbers representing the optical activity and reducing power correspond exactly with those afforded by a *mixture* of maltose and dextrin, and the results can be expressed as above in terms of these compounds. In this respect, amylo-dextrin, although a product of the action of *acid* upon starch, conforms to the rule we established experimentally (Trans., 1885, 47, 538) for any fractionated portion of the products obtained by the action of malt-extract or diastase on starch-paste. It is evident that the dextrose-group cannot enter into its composition.

Although its crystalline nature rendered it in the highest degree probable that amylo-dextrin was a definite compound, it seemed desirable to make every possible attempt to differentiate it. We have consequently treated it in very much the same way as we did maltodextrin, described in the paper just quoted.

Amylo-dextrin is absolutely unfermentable by the *Saccharomyces cerevisiae* of the high fermentation, consequently its cupric-reducing constituent cannot exist in the state of free maltose.

On attempting to fractionate solutions of pure amylo-dextrin by throwing it down with alcohol of gradually increasing strength, it

\* The percentage composition deduced from actual weights of substance would be identical with the results obtained by the use of the 3.86 divisor, provided we employed for dextrin and maltose the constants also deduced from actual weight.

was found that precipitation takes place so completely, and within such sharply defined limits of alcoholic percentage, that it is practically impossible to effect any fractional separation in this manner.

Not the slightest differentiation could be effected by the method of partial solution, employing cold water as the medium, in which it is soluble to the extent of about 1.75 per cent.

The same is also true with regard to dialysis. Contrary to the assertions of W. Nägeli, we find that amyloextrin is sensibly but slowly diffusible.

150 c.c. of a solution containing 14.660 grams per 100 c.c. were put into a plicated parchment-paper dialyser, supported by a Nickel's funnel, and exposing an effective diffusion surface of about 30 square inches. The water outside the dialyser was changed five times at intervals of about 24 hours. At the end of five days, the diffusates were evaporated to 90 c.c., and contained 2.75 grams of substance, which on analysis gave the following numbers:—

$[\alpha]_{j3.86}$ .....	204.6°
$\kappa_{3.86}$ .....	10.12

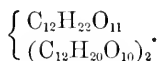
corresponding to a composition of—

Maltose ....	16.60	} which re-	{ $[\alpha]_{j3.86}$ ....	205.0°
Dextrin ....	83.40			
	<hr/>			
	100.00			

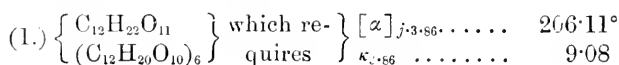
A comparison of these numbers with those given for pure amyloextrin shows that no differentiation has taken place, the substance having passed through the dialyser unchanged.

The above considerations, coupled with the truly crystalline nature of the substance, lead us irresistibly to the conclusion that in amyloextrin we have to deal with a perfectly homogeneous compound of definite composition.

It is doubtless a compound closely analogous to the maltodextrin we described in 1885 (*loc. cit.*), and which we were led to regard as made up of two amylin- or dextrin-groups in combination with a maltose-group, thus:—



The simplest formula which we can assign to amyloextrin is either that represented by six dextrin- or *amylin*-groups in combination with one maltose- or *amylon*-group, thus:—



or a formula represented by five dextrin- or *amylin*-groups, in combination with one maltose- or *amylon*-group, thus—

$$(2.) \left\{ \begin{array}{l} \text{C}_{12}\text{H}_{22}\text{O}_{11} \\ (\text{C}_{12}\text{H}_{20}\text{O}_{10})_5 \end{array} \right\} \text{ which re- } \left\{ \begin{array}{l} [\alpha]_{j3,86} \dots\dots 204.5^\circ \\ \kappa_{j3,86} \dots\dots\dots 10.6 \end{array} \right.$$

The actual numbers obtained for amylopectrin, viz. :—

$$\begin{array}{ll} [\alpha]_{j3,86} \dots\dots\dots & 206.25 \\ \kappa_{j3,86} \dots\dots\dots & 9.07 \end{array}$$

leave little doubt that formula No. 1 is the correct one, and this was strikingly confirmed by the estimation of the molecular weight of amylopectrin by Raoult's method,\* which yielded the following numbers :†—

I. Freezing point of water used,  $+0.025^\circ$ .

Strength of solution, 10.159 grams amylopectrin in 93.87 grams water :—

E.	C.	A.	M.
$-0.070^\circ$	$0.095^\circ$	0.0087	2185
$-0.070$	$0.095$	0.0087	2185

II. Freezing point of water used,  $+0.060^\circ$ .

Strength of solution, 8.622 grams amylopectrin in 94.80 grams water.

E.	C.	A.	M.
$-0.015^\circ$	$0.075^\circ$	0.0083	2290

Mean of the above results—

$$\begin{array}{ll} A = \text{coefficient of depression} \dots & 0.0086 \\ M = \text{molecular weight} \dots\dots\dots & 2220 \end{array}$$

Whilst the molecular weight of  $\left\{ \begin{array}{l} \text{C}_{12}\text{H}_{22}\text{O}_{11} \\ (\text{C}_{12}\text{H}_{20}\text{O}_{10})_6 \end{array} \right\}$  is 2286,

and that of  $\left\{ \begin{array}{l} \text{C}_{12}\text{H}_{22}\text{O}_{11} \\ (\text{C}_{12}\text{H}_{20}\text{O}_{11})_5 \end{array} \right\}$  is 1962.

We must consequently look upon the first formula as the correct one, and must regard the amylopectrin molecule as being made up of six *amylin*-groups united with one *amylon*-group.

We find that amylopectrin, like maltodextrin, is converted rapidly and completely into *maltose* under the action of diastase, as is well shown in the following experiments.

\* It was found that the property which amylopectrin possesses of separating from its solutions at a low temperature did not prove any obstacle to the employment of this method, owing to the slowness of the separation.

† For details of the method, and for an explanation of the terms employed, see our former paper (Trans., 1888, 53, 610).

A solution containing 6.756 grams of amylo-dextrin per 100 c.c. was treated with a little diastase for 60 minutes at 55°. The product gave the following numbers:—

		Maltose requires.
$[\alpha]_{j3.86}$ . . . . .	151.7°	150.4°
$\kappa_{j3.86}$ . . . . .	61.54	60.8

This rapid hydrolysis to maltose is also very clearly shown when the solution of amylo-dextrin used in the second experiment for the determination of molecular weight was degraded with a little diastase and again treated by Raoult's method.

The amount of diastase used in the experiment was 0.327 gram per 100 c.c. The action was allowed to continue for 60 minutes in the cold.

Freezing point of a solution of diastase containing the above amount +0.045°.

Strength of solution, 9.4508 grams in 94.19 gram water.

E.	C.	A.	M.
-0.495°	0.540°	0.054	352
-0.495	0.540	0.054	352

Tabulating the properties of the substance in solution before and after treatment with diastase, we find them as follows:—

	(1) Before treatment with diastase.	(2) After treatment with diastase.
$[\alpha]_{j3.86}$ . . . . .	205.3°	150.7°
M (molecular weight) =	2290	352

The actual numbers for maltose are—

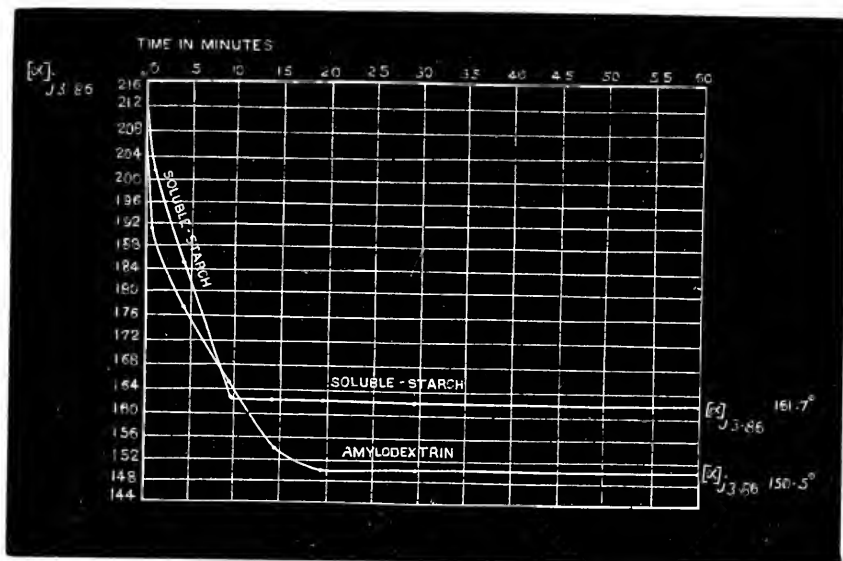
$[\alpha]_{j3.86}$ . . . . .	150.4°
M . . . . .	342

The difference in behaviour between soluble starch and amylo-dextrin under the action of diastase is well shown in the following time experiments, which are expressed both numerically and graphically. It will be noticed that the resting point in the reaction with soluble starch, to which frequent reference has been made in previous papers, is extremely well marked; whereas in the case of amylo-dextrin *no such halt is apparent*, the hydrolysis progressing uninterruptedly to maltose.

The two substances are compared under identically similar conditions, the reaction taking place in the cold.

Time in minutes.	(1.) Soluble starch.	(2.) Amylodextrin.
	$[\alpha]_{D^{20}}^{25}$	$[\alpha]_{D^{20}}^{25}$
—	215.0°	205.3°
1	202.2	190.3
5	185.2	178.7
10	163.9	165.1
15	161.7	153.5
20	161.7	150.5
30	161.7	150.5
60	161.7	150.5

FIG. 1.—Showing the Degradation of Soluble Starch and Amylodextrin by Diastase, under similar conditions.



It is very evident that amylopectin cannot contain the highly stable amylin or dextrin nucleus which constitutes one-fifth of the soluble starch molecule, and which is capable of resisting for a considerable time the action of diastase. This amylin-group must have been hydrolysed by the acid during the long-continued digestion.

The successive chemical changes which take place during the transformation of the starch-granules into amylopectin under the action of dilute acids now claim our attention.

We have already seen that the first step is the conversion of the starch substance into soluble starch, without any alteration in its organisation.

We give below the details of the analysis of the residual starch at various stages, and also the effect of "degrading" these residues, that is, of hydrolysing them with diastase until the point of equilibrium is reached. If we bear in mind that, under these circumstances, soluble starch is degraded to a point at which the mixed products of transformation have a composition of—

Maltose.....	80.9	} correspond-	{	$[\alpha]_{j3.86} \dots$	162.6°	
Dextrin .....	19.1			ing to	$\kappa_{3.86} \dots\dots$	49.3
<hr/>						
100.0						

and that amyloextrin, on the other hand, is degraded down to *maltose*, it will be evident that the results indicate a slow and gradual hydrolysis of the first formed soluble starch to amyloextrin.

*Analysis of Residual Substance after Digestion of Potato-starch for different periods in Hydrochloric Acid of 11 per cent.*

(1.) After 48 hours.

$[\alpha]_{j3.86} \dots$	216.0°
$\kappa_{3.86} \dots$	0.56

After degradation with diastase.

$[\alpha]_{j3.86} \dots$	162.06°	Maltose..	81.41	} re- quires	{	$[\alpha]_{j3.86} \dots$	162.2°
$\kappa_{3.86} \dots$	49.66	Dextrin.	18.59			$\kappa_{3.86} \dots$	49.66

At this stage the residue consisted of almost pure soluble starch, yielding almost exactly the theoretical numbers on treatment with diastase. The granules still retained their organisation, and were coloured a deep, pure blue with iodine.

(2.) After 12 days.

$[\alpha]_{j3.86} \dots$	209.2°
$\kappa_{3.86} \dots$	2.78

After degradation with diastase.

$[\alpha]_{j3.86} \dots$	161.6°	Maltose..	87.7	} re- quires	{	$[\alpha]_{j3.86} \dots$	158.1°
$\kappa_{3.86} \dots$	53.52	Dextrin..	12.3			$\kappa_{3.86} \dots$	53.52

---

100.0

The granules were unaltered in microscopical appearance. Iodine coloured them a reddish-purple.

(3.) After 21 days.

$[\alpha]_{j3.86} \dots$	210.2°
$\kappa_{3.86} \dots$	3.24



After degradation with diastase.						
$[\alpha]_{j3,86} \dots$	161.2°	Maltose..	85.77	} re-quires	$[\alpha]_{j3,86} \dots$	159.3°
$\kappa_{3,86} \dots$	52.32	Dextrin..	14.23		$\kappa_{3,86} \dots$	52.32
					<hr/> 100.00	

Nearly all the granules had split across their shorter diameter, and were coloured a light reddish-brown by iodine.

(4.) After 33 days.

$[\alpha]_{j3,86} \dots$	208.4°
$\kappa_{3,86} \dots$	4.4

After degradation with diastase.						
$[\alpha]_{j3,86} \dots$	160.7°	Maltose..	90.1	} re-quires	$[\alpha]_{j3,86} \dots$	156.5°
$\kappa_{3,86} \dots$	54.96	Dextrin..	9.9		$\kappa_{3,86} \dots$	54.96
					<hr/> 100.0	

Iodine reaction the same as in (3), but some of the granules began to show signs of disintegration.

(5.) After 66 days.

$[\alpha]_{j3,86} \dots$	205.5°
$\kappa_{3,86} \dots$	6.05

After degradation with diastase.						
$[\alpha]_{j3,86} \dots$	157.2°	Maltose..	92.65	} re-quires	$[\alpha]_{j3,86} \dots$	155.2°
$\kappa_{3,86} \dots$	56.15	Dextrin..	7.95		$\kappa_{3,86} \dots$	56.15

All the granules were at this stage strongly acted upon, and showed marked signs of disintegration along their lines of stratification.

(6.) After 100 days.

$[\alpha]_{j3,86} \dots$	206.0°
$\kappa_{3,86} \dots$	6.95

After degradation with diastase.						
$[\alpha]_{j3,86} \dots$	157.3°	Maltose..	92.24	} re-quires	$[\alpha]_{j3,86} \dots$	155.2°
$\kappa_{3,86} \dots$	56.27	Dextrin.	7.76		$\kappa_{3,86} \dots$	56.27
					<hr/> 100.00	

The granules at this stage had been so far disintegrated as to retain but little of their original form.

It is evident that even after 100 days' digestion the experiment had not been carried on sufficiently long to convert the whole of the soluble starch into amylopectin, and a subsequent examination of the product confirmed this.

It is probable that, under the conditions of the experiment, a period of from five to six months is necessary for the complete conversion. We have already described the properties of the substance yielded by a digestion of several years, but we will again introduce the numbers obtained for the sake of comparison.

(7.) After  $8\frac{1}{2}$  years.

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On dissolving in water and reprecipitating with alcohol, pure amylo-dextrin was obtained.

		After degradation with diastase.			
[ $\alpha$ ] <sub>j3, ∞6</sub> . .	205.3°	[ $\alpha$ ] <sub>j3, ∞6</sub> . .	151.7°	} maltose.	
$\kappa$ <sub>3, ∞6</sub> . . . .	9.92	$\kappa$ <sub>3, ∞6</sub> . . . .	61.54		

On examination of the acid solution (dilute  $\text{H}_2\text{SO}_4$ ) which had been in contact with the starch for  $8\frac{1}{2}$  years, it was found to contain an amount of substance corresponding to about 40 per cent. of the original weight of starch taken. That this substance was *dextrose* is shown by the following analysis, which was made after neutralisation of the acid in the cold with barium carbonate:—

	Found.	Dextrose requires.
[ $\alpha$ ] <sub>j3, ∞6</sub> . . . . .	57.36	58.6°
$\kappa$ <sub>3, ∞6</sub> . . . . .	97.49	100.00

The dextrose was readily separable by crystallisation.

#### General Conclusions.

(1.) One of the final products of the action of dilute mineral acids upon ungelatinised starch in the cold is the *amylo-dextrin* described by W. Nägeli in 1874.

(2.) Although its composition may be expressed in terms of maltose and dextrin, amylo-dextrin is not a mixture of these substances, but is a well-defined chemical substance. This is shown (a) by its absolute unfermentability with the ordinary yeast of the top fermentation; (b) by the impossibility of differentiating it by fractional precipitation or partial solution; (c) by its passage through

the dialyser in an unaltered form; and (*d*) by its distinct crystalline nature.

(3.) Amylodextrin does not possess the optical properties ascribed to it by its discoverer. Its specific rotatory power is  $[\alpha]_{3.86} = 206.11^\circ$ , instead of  $[\alpha] = 175^\circ$  to  $177^\circ$ , as stated by Nægeli. Its power of reducing cupric oxide is represented by  $\kappa_{3.86} = 9.08$ .

(4.) In composition, amylodextrin is analogous to the maltodextrin we have previously described (Trans., 1885, **47**, 528). It may be represented by the formula  $\left\{ \begin{array}{l} \text{C}_{12}\text{H}_{22}\text{O}_{11} \\ (\text{C}_{12}\text{H}_{20}\text{O}_{10})_6 \end{array} \right.$ , that is, as constituted of one *amylon*- or maltose-group in combination with six *amylin*- or dextrin-groups. The molecular weight found by Raoult's method is entirely in accordance with this formula.

(5.) Amylodextrin, like maltodextrin, is hydrolysed by diastase immediately to maltose without any indications of a resting point in the reaction; it cannot, therefore, contain the stable amylin nucleus which constitutes one-fifth of the molecule of soluble starch, and which is only with difficulty attacked by diastase.

(6.) Amylodextrin is an entirely different substance from soluble starch, with which it has been confounded by most observers.

(7.) When ungelatinised starch is acted upon by dilute mineral acids in the cold, the first action is to convert the starch-substance of the granules into soluble starch; this is then gradually hydrolysed to *amylodextrin*, a portion at the same time going into solution, and being ultimately found as *dextrose*.

*Note.*—The insoluble portion which remains after the treatment of starch-paste with malt-extract in the cold, has been erroneously considered by A. Meyer to be identical with amylodextrin. ("Ueber die wahre Natur von Nægeli's Stärkecellulose," *Botan. Zeit.*, 1886, 356.) This substance was fully described by one of us and Heron some years ago (*Chem. Soc. J.*, **35**, 611, 1879), and, following Nægeli, we regarded it as starch-cellulose. The properties of the so-called starch-cellulose are entirely different from those of amylodextrin, as will be seen by reference to the paper just quoted; but whether we are to consider it as a true cellulose, pre-existent in the starch-granule, or as a transformation product of the starch substance, is a question which we must for the present leave an open one.

XIV.—*The Determination of the Molecular Weights of the Carbohydrates.* Part II.

By HORACE T. BROWN, F.R.S. and G. HARRIS MORRIS, Ph.D., F.I.C.

IN the first part of this paper (*Chem. Soc. J.*, Trans., 1888, **53**, 610), we laid before the Society the results which we had obtained by the application of Raoult's method to the determination of the molecular weights of some of the carbohydrates, and showed how the numbers obtained were, generally speaking, in close accord with those commonly accepted as expressing these values, and also that the method was capable in some cases, notably in those of *arabinose* and *raffinose*, of deciding between the two or more doubtful formulæ.

During the last year, Raoult's method has been largely employed by chemists for very varied classes of compounds, and where it has been possible to compare the results with those obtained by the vapour-density method, there has been, on the whole, such a remarkable correspondence as to justify an increased confidence in the wide applicability of the method.

Almost simultaneously with the appearance of our first paper, Tollens and Mayer (*Ber.*, **21**, 1566, 1888) determined the molecular weights of raffinose, dextrose, cane-sugar, and milk-sugar by the freezing method, and arrived practically at the same numbers as we have given for those compounds. Tollens, Mayer, and Wheeler have also more recently (*Ber.*, **21**, 3508, 1888) confirmed our numbers for arabinose, and have determined the molecular weight of xylose.

De Vries (*Compt. rend.*, **106**, 751, and *Zeit. physikal. Chem.*, **2**, 431) has applied successfully to raffinose a totally different method, which is based upon a determination of the osmotic pressure of solutions. The investigations of De Vries and Van't Hoff have shown that solutions of similar osmotic pressure have the same freezing point and the same vapour pressure. Such solutions are said to be isotonic to each other. De Vries determines the molecular weight of a given substance by comparing its isotonic concentration with that of another substance of known molecular weight, and belonging to the same osmotic group. The isotonic concentration is measured in a very beautiful manner microscopically, by determining the strength of solution necessary to *plasmolyse* certain turgescient vegetable cells; that is, to cause a separation of the protoplasmic membrane from the cell-wall by outward diffusion of the water of the cell-sap into the solution under experiment. In this manner, De Vries has obtained for raffinose numbers indicative of a molecular weight of 595·7, almost the theoretical requirements of the formula  $C_{15}H_{32}O_{16}\cdot 5H_2O$ , and agreeing

very closely with the results we obtained for raffinose by the freezing method.

We have now to describe the results obtained by a further examination of certain substances belonging to the group of carbohydrates.

The method of experiment was substantially the same as that described in the first part of this paper. We have used, however, in our later experiments a thermometer graduated to  $\frac{1}{50}$  of a degree centigrade, and capable of being read accurately to 0.004 of a degree.

*Galactose*,  $C_6H_{12}O_6$ ,  $M = 180$ .

This sugar is one of the products of the hydrolysis of milk-sugar,  $C_{12}H_{22}O_{11}$ , with dilute acid, the other product being dextrose.

It was crystallised from alcohol and dried in a vacuum. For a solution containing 10 grams of galactose per 100 c.c. we found—

$[\alpha]_j$ at 19° C. ....	89.47°
$[\alpha]_D$ at 19° C. ....	80.69

Freezing point of water used +0.060°.

Strength of solution 10.000 grams galactose in 93.87 grams water.

E.*	C.	A.	M.
—1.090°	1.150°	0.108	176
—1.080	1.140	0.107	177.5
—1.080	1.140	0.107	177.5
	Calculated for $C_6H_{12}O_6$ .	Found (mean).	
A .....	0.106	0.1073	
M .....	180.0	177.0	

*Inulin*,  $nC_6H_{10}O_5$ , or  $C_{36}H_{62}O_{31}$ .

The formula which has been usually accepted for inulin is  $nC_6H_{10}O_5$ , but the careful researches of Kiliani (*Annalen*, **205**, 145) certainly indicate that it yields on combustion a smaller amount of carbon and a larger amount of hydrogen than is compatible with this formula. His numbers for the pure substance dried at 100—130° are extremely concordant, and are given in great detail in his paper. They point unmistakably to a formula whose simplest expression is  $C_{36}H_{62}O_{31}$  or  $6C_6H_{10}O_5 + H_2O$ , and this composition is unaltered even after drying at 130° in a stream of hydrogen.

The results obtained by treating inulin by Raoult's method are as follows, the substance having been previously dried at 100° until it ceased to lose weight.

\* For explanation of these headings, see first part of this paper (*Trans.*, 1888, **53**, 614).

Freezing point of water used  $+0.060^{\circ}$ .

15.079 grams inulin in 91.9 grams water.

E.	C.	A.	M.
$-0.084^{\circ}$	$0.144^{\circ}$	0.0088	2159

A second determination was made after further purifying by solution in water and precipitation by alcohol.

Freezing point of water used  $+0.120^{\circ}$ .

17.614 grams inulin in 105.7 grams water.

E.	C.	A.	M.
$-0.024^{\circ}$	$0.144^{\circ}$	0.0086	2209
$-0.026$	0.146	0.0088	2159

Molecular weight  
calculated for

$C_{36}H_{62}O_{31}$	M . . . . .	990.0
$2C_{36}H_{62}O_{31}$	M . . . . .	1980.0
$3C_{36}H_{62}O_{31}$	M . . . . .	2970.0

Our experiments, we consider, justify us in attributing to inulin a formula represented by twice that given by Kiliani, that is,  $2C_{36}H_{62}O_{31}$ .

We have already drawn attention in a previous paper to the great similarity, as regards their physical properties, between amyloextrin and inulin. We now know that they are compounds possessing approximately the same molecular weight, and from a consideration of all the facts, we are inclined to regard inulin as a substance closely analogous to amyloextrin in its composition, and should attribute to the two compounds the following formulæ:—

$\left\{ \begin{array}{l} (C_{12}H_{22}O_{11})_2 \\ (C_{12}H_{20}O_{10})_4 \end{array} \right.$	$\left\{ \begin{array}{l} C_{12}H_{22}O_{11} \\ (C_{12}H_{20}O_{10})_8 \end{array} \right.$
Inulin.	Amyloextrin.
M = 1980.	M = 2286.

The amylin- and amylo-groups in the two compounds possess very different optical properties, and behave differently with regard to cupric reduction. The ultimate products of hydrolysis with dilute acids are also very different, being in the one case levulose and in the other dextrose.\*

For the details of the determination of the molecular weight of amyloextrin we must refer to the previous paper.

\* If our views on these points are correct, it would follow that inulin is a product of hydrolysis of an unknown carbohydrate, and stands in the same general relation to this substance as does amyloextrin to starch. That inulin is not directly hydrated to levulose by dilute acid, but that a series of intermediate compounds is produced, is rendered highly probable by the experiments of Dragendorff, and more recently by those of Green (*Ann. Bot.*, 1888).

$$\text{Maltodextrin}, \left\{ \begin{array}{l} \text{C}_{12}\text{H}_{22}\text{O}_{11} \\ (\text{C}_{12}\text{H}_{20}\text{O}_{10})_2 \end{array} \right\}, M = 990.$$

In a previous paper (Trans., 1885, 560), we have described this compound as occurring amongst the transformation products of starch when the action of the hydrolysing agent, diastase, is limited.

The specific rotatory and cupric reducing powers of pure maltodextrin are represented by—

$$\begin{array}{ll} [\alpha]_{j3.86} & \dots\dots\dots 193.1^\circ \\ \kappa_{3.86} & \dots\dots\dots 21.1 \end{array}$$

and we were led to consider it as being made up of one amylo-n group in combination with two amylin-groups.

A determination of the molecular weight of maltodextrin by Raoult's method is entirely in accordance with this view, as is shown by the following results:—

Freezing point of water used,  $0.060^\circ$ .

Strength of solution, 8.6114 grams maltodextrin in 94.71 grams water.

E.	C.	A.	M.
$-0.118^\circ$	$0.178^\circ$	$0.0195$	$974$
$-0.120$	$0.180$	$0.0198$	$960$
$-0.120$	$0.180$	$0.0198$	$960$

	Calculated for	Found
	$\left\{ \begin{array}{l} \text{C}_{12}\text{H}_{22}\text{O}_{11} \\ (\text{C}_{12}\text{H}_{20}\text{O}_{10})_2 \end{array} \right\}$	(mean).
A .....	$0.0191$	$0.0197$
M .....	$0.990$	$0.965$

#### *Starch*, $n(\text{C}_{12}\text{H}_{20}\text{O}_{10})$ .

Owing to the very viscid nature of starch-paste, and the great increase in this viscosity at low temperatures, it is absolutely impossible to apply to it Raoult's method. Our direct experiments on this carbohydrate were consequently limited to the modification known as *soluble starch*, which was prepared in a pure state by Liutner's method, referred to in our paper on amylo-dextrin.

Notwithstanding the complete limpidity of solutions of soluble starch at ordinary temperatures, these also become viscid on cooling to  $0^\circ$ , if they are of any considerable degree of concentration, and it was consequently found impossible to operate with a solution containing more than 3.5 grams per 100 c.c.

Although separate experiments gave fairly concordant values for A of about 0.0009 corrected, which corresponds to a molecular weight of 20,000 to 30,000, the errors of experiment bear so large a propor-

tion to the observed readings that it is impossible to place any great amount of dependence on the results, no matter how carefully the experiments are conducted.

There also seemed a possibility that the method was not applicable to substances of such a highly colloïd nature as starch.

In order to throw some light upon this last-named point, we made some experiments with another colloïdal body, an arabinic acid possessing a right-handed rotation of  $[\alpha]_j = 61.16^\circ$ . This gave the following results:—

Freezing point of water used,  $+0.060$ .

11.928 grams arabinic acid in 92.50 grams water.

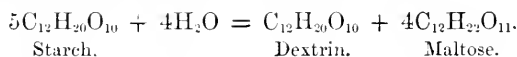
E.	C.	A.	M.
$-0.310^\circ$	$0.340^\circ$	$0.0263$	$7.22$
$-0.315$	$0.345$	$0.0267$	$7.12$

We see that arabinic acid, a substance with strongly marked colloïdal properties, has a marked influence in lowering the freezing point; hence it seemed probable that the small influence observed in the case of soluble starch is really due to the large size of its molecule.

Since it is impossible to obtain with soluble starch in a direct way any numbers which can be regarded as even fair approximations to the truth, we were necessarily driven to more indirect methods, which have afforded more satisfactory results.

When the complex molecule of starch is broken down by diastase under the conditions most favourable to its complete hydrolysis, we have shown that a point of equilibrium, or, speaking more strictly, a resting point in the reaction is reached, when the amount of dextrin produced corresponds to *one-fifth* by weight of the amount of starch taken; that is, when the mixed products have  $[\alpha]_{j3.56} = 162.6^\circ$  and  $\kappa_{3.56} = 49.3$ .

This reaction is expressed in its simplest form by—



If the production of maltose and dextrin during hydrolysis is to be considered as due to a molecular degradation of the starch, and we think the evidence in favour of this is almost conclusive;\* then, no matter what view we may take of the actual manner in which this degradation takes place, we cannot escape from the conclusion that *the molecule of the stable dextrin of the above equation is one-fifth of the size of the soluble starch molecule from which it has been derived.*

\* Cf. Appendix to this paper.



If, then, we can establish the size of the molecule of this lowest and most stable dextrin we can indirectly determine the size of the starch molecule. Our endeavours have consequently been directed towards determining this point, and, as will be seen, not without success.

A conversion of starch with diastase was allowed to run down to its lowest limit, as stated above, and the resulting dextrin was separated by repeated precipitation with alcohol until the greater part of the maltose had been removed. On analysis the dextrin gave the following numbers:—

$$\begin{array}{rcccl} [\alpha]_{j3.86} \dots & 209.3^\circ & \text{Maltose..} & 8.16 & \} \text{ re-} \left\{ [\alpha]_{j3.86} \dots & 210.6^\circ \right. \\ \kappa_{j3.86} \dots\dots & 4.98 & \text{Dextrin..} & 91.84 & \} \text{ quiring} \left\{ \kappa_{j3.86} \dots\dots & 4.98 \right. \\ & & & \hline & & & 100.00 & & \end{array}$$

A freeze was made with this dextrin.

Freezing point of water used  $+0.060^\circ$ .

(1.) 6.788 grams of dextrin in 95.90 grams of water.

E.	C.	A.	A'.	M.
$+0.008^\circ$	$0.052^\circ$	0.0073	0.0031	6333

\* A' represents the coefficient of depression of the dextrin after correction for the maltose present. This mode of correcting the results can of course only be accurate if the total effect of a mixture of substances in depressing the freezing point is the sum of the effect of each constituent taken separately. This has already been shown to be the case by Raoult, but it seemed advisable to confirm it for the carbohydrates.

Solutions were made of (1) dextrose, (2) cane-sugar, and (3) a mixture of these two substances.

(1.) *Dextrose.*

Freezing point of water used,  $+0.085^\circ$

11.295 grams in 93.06 grams water.

E.	C.	A.	M.
$-1.255^\circ$	$1.340^\circ$	0.110	173

(2.) *Cane-sugar.*

13.717 grams in 91.57 grams water.

E.	C.	A.	M.
$-0.820^\circ$	$0.905^\circ$	0.060	316

(3.) *Dextrose and Cane-sugar.*

5.647 grams dextrose }  
6.858 „ cane-sugar } in 92.32 grams water.

12.505

E.	C.	A'.	M'.
$-1.040^\circ$	$1.125^\circ$	0.083	231

Value of M' calculated from actual molecular weight of constituents .. 260.8

(2.) 17.758 grams of same dextrin as in (1), in 89.29 grams water.

E.	C.	A.	A'.	M.
-0.088°	0.148°	0.0074	0.0031	6130
-0.088	0.148	0.0074	0.0031	6130
-0.088	0.148	0.0074	0.0031	6130

Another low dextrin prepared in a similar manner gave the following results:—

*Analysis.*

$[\alpha]_{j3, \infty 6} \dots$	211.3°	Maltose..	9.7	} re-quiring {	$[\alpha]_{j3, \infty 6} \dots$	209.5°
$\kappa_{3, \infty 6} \dots$	5.87	Dextrin..	90.3		$\kappa_{3, \infty 6} \dots$	5.87
						100.0

Freezing point of water, +0.060°.

20.743 grams dextrin in 87.50 grams water.

E.	C.	A.	A'.	M.
-0.130°	0.190°	0.0080	0.0030	6333
-0.135	0.195	0.0082	0.0032	5937
-0.130	0.190	0.0080	0.0030	6333

Another low dextrin prepared in a similar manner gave—

*Analysis.*

$[\alpha]_{j3, \infty 6} \dots$	208.6°	Maltose..	9.06	} re-quiring {	$[\alpha]_{j3, \infty 6} \dots$	211.1°
$\kappa_{3, \infty 6} \dots$	5.53	Dextrin .	91.94		$\kappa_{3, \infty 6} \dots$	5.53
						100.00

Freezing point of water, +0.060°.

30.2217 grams dextrin in 81.78 grams water.

E.	C.	A.	A'.	M.
-0.250°	0.310°	0.0078	0.0030	6333
-0.250	0.310	0.0078	0.0030	6333

The mean value of M in these experiments with the lowest dextrin is 6221, and the numbers obtained have but a small range on either side of this mean. The formula  $20C_{12}H_{20}O_{10}$  requires a molecular weight of 6480; and we think the experimental evidence quite justifies us in adopting this value.

The formula of soluble starch would consequently be represented by five times the above, that is,  $5(C_{12}H_{20}O_{10})_{20}$ , and the molecular weight by 32,400.

This is quite in accordance with the approximation obtained in a direct way with soluble starch, where, it will be remembered, we

obtained indications of a molecular weight somewhere between 20,000 and 30,000.

We have now to consider if Raoult's method is able to throw any light on the relations of the dextrans to each other, as it is a matter of the highest theoretical importance to determine whether these bodies constitute a series of polymers, or whether they stand merely in metamerie relation to each other.

In order to determine this point, we have prepared a number of the higher dextrans proceeding from starch-transformations which had been stopped in an early stage of hydrolysis.

It will be unnecessary to give the full details of every experiment; the following may, however, be quoted as an example:—

*Analysis.*

$[\alpha]_{j3,86} \dots$	210.7	Maltose ..	2.3	} re-	{	$[\alpha]_{j3,86} \dots$	214.4°
$\kappa_{3,86} \dots$	1.4	Dextrin ..	97.7			quiring	$\kappa_{3,86} \dots$

In the accompanying table, we give the experimental results obtained on submitting some of the dextrans to the freezing method. The position occupied by each dextrin in the series, as measured by its maximum degradation with diastase, is given in the sixth column.

A comparison of the results obtained with the so-called high and low dextrans points unmistakably to the conclusion that Raoult's method affords no evidence of there being any difference in molecular size between the high and the low dextrans; in fact, the numbers obtained with dextrans occupying very different positions in the series are strikingly identical. It must be remembered, however, that at present our knowledge of the behaviour of polymers when submitted to this method is not sufficiently advanced for us to say with certainty that it is applicable to a determination of molecular aggregates such as we imagine the dextrans to be.

It has been suggested by Armstrong (*Brit. Assoc. Rep.*, 1888, 357) that Raoult's method may, after all, only afford evidence of molecular complexity when some atomic rearrangement has taken place, as in the case of aldehyde and paraldehyde; and that it may not give any indication of the size of a molecular complex formed by the mere juxtaposition of molecules. We think, however, that this criticism of the applicability of the method scarcely touches the case with which we are dealing, and for the following reasons:—

As far as our present knowledge goes, there is not the slightest evidence to indicate that the mode of connection between the amylin-groups of soluble starch differs in kind from that between the amylin-groups of the dextrans—supposing these last to be polymers. If there is atomic rearrangement in one case, there is no reason why it should not be present in the other; if, on the other hand, it is a mere juxtaposition of molecules in one case, why not in the other? In fact there is every reason to believe that the mode of union between the component groups would be the same in both cases. If, therefore, Raoult's method gives us direct evidence—as it undoubtedly does—of a great difference in molecular size between soluble starch and the dextrans, we should also expect it to indicate differences in the molecular size of the dextrans themselves, if these really existed, and if the dextrans are produced by a gradual breaking down and decrease in size of the starch-molecule, with polymerisation of the residual amylin-groups.

That Raoult's method does not indicate these differences, when the various dextrans are treated by it, goes in our opinion a long way dextrans to be due wholly or in part to maltodextrans, the corrected value of  $M$  for the dextrin will be somewhat *smaller* than that given: consequently, the arguments based upon this and the following experiments are not in any way altered by the fact.

No.	Analysis of substance,		Percentage composition,		Degradation,		Strength of solution used,		Observed $\alpha$ .	Corrected $\alpha$ .	M of dextrin.
	$[\alpha]_{D^{20}}$	$\kappa_{D^{20}}$	Dextrin.	Maltose.	100 parts dextrin gave maltose.	Mean position of dextrin.	Grams substance.	Grams water.			
1.....	209.5	5.87	90.30	9.70	0	8	20.7430	87.50	0.0080	0.0039	6333
2.....	209.3	4.98	91.84	8.16	0	8	6.7880	95.90	0.0073	0.0030	6333
3.....	—	—	—	—	0	8	17.7580	89.29	0.0075	0.0032	5937
4.....	208.6	5.53	91.94	9.06	0	8	30.2217	81.78	0.0078	0.0030	6333
5.....	199.8	12.60	79.40	20.60	0	8	18.0900	88.52	0.0139	0.0032	5937
6.....	—	—	—	—	0	8	9.6666	94.23	0.0132	0.0029	6552
7.....	210.7	1.40	97.70	2.30	71.5	3—4	33.1005	77.96	0.0043	0.0031	6129
8.....	206.9	6.45	89.50	10.50	70.0	4	19.6040	88.18	0.0087	0.0032	5937
9.....	210.3	3.94	93.54	6.46	52.8	6	19.5640	88.20	0.0063	0.0030	6333
10.....	202.1	13.90	77.10	22.90	81.5	0	16.3730	90.12	0.0148	0.0030	6333

towards proving that, after all, the dextrans are metameric and not polymeric. If this is admitted as even probably correct, it becomes necessary to consider how far our previous views on the breaking down of the starch-molecule must be modified in order to include the new facts.

In a previous paper by one of us and Heron (Trans., 1879, **35**, 646), we considered that the very simplest formula which could be adopted for soluble starch was  $10C_{12}H_{20}O_{10}$ , and that during hydrolysis by diastase each of these 10 amylin-groups was successively removed in the form of maltose, whilst the remaining amylin-groups polymerised to form a dextrin of gradually decreasing complexity—the last dextrin of the series being one-fifth of the original starch-molecule.

In a more recent paper (Brown and Morris, Trans., 1885, **47**, 527), after an investigation of maltodextrin and a determination of its relation to starch and the dextrans, we noted that the original hypothesis was insufficient to include all the new facts which were then brought forward, and suggested, as a useful working hypothesis, an extension of the original idea, stating, at the same time, that we were far from regarding it as final, and that it would doubtless require still further development as a more intimate knowledge of the subject was gained.

We suggested, in the paper just referred to, that the starch-molecule could not be looked upon as consisting of less than five times the ternary group  $(C_{12}H_{20}O_{10})_3$ . We were still inclined to believe that the action of diastase in hydrolysing the above molecule consisted in successive hydrations and removals of  $(C_{12}H_{20}O_{10})_3$ -groups through maltodextrin to maltose, whilst the dextrin residues polymerise until the hydrolysis has proceeded so far as to reach the stage of the lowest dextrin—which only undergoes further change by a comparatively slow process of hydration.

It is evident that the above views require considerable modification if the so-called high and low dextrans are bodies possessing the same molecular weight, and we have now to consider how an alternative hypothesis can be framed which will enable us to explain the known differences in the properties of the dextrans without at the same time regarding them as polymers.

O'Sullivan, in 1879 (Trans., **35**, 783), stated his belief that the breaking down of the starch molecule by diastase did not result in the successive appearance of dextrin molecules becoming smaller at each step, and "that we have not, in this case, to do with a series of polymerides, but rather with a series of bodies of the same molecular weight, in which the difference in their behaviour to the agent under consideration must be accounted for by a difference of *relation in*

*the arrangement of the molecules to one another, probably in solution alone."*

O'Sullivan regards the molecule of soluble starch as being identical in complexity with the molecules of the various dextrans, the groups of molecules rearranging themselves during the transformation so as to maintain the resulting dextrin molecule always of the same size. For the elaboration of this hypothesis, and for an explanation of how this rearrangement is supposed to take place, we must refer to the original paper (*loc. cit.*).

The new facts which we have brought forward, whilst confirming O'Sullivan's view as to the identity in molecular size of the dextrans, indicate, on the other hand, that the molecule of soluble starch must be of much greater complexity than that of the dextrans, and that we must seek for some other explanation of the phenomena of starch transformations than is afforded by the above elaborate hypothesis of molecular rearrangement.

The following hypothesis seems to us to be more in accord with the facts.

We may picture the starch-molecule as consisting of four complex amylin-groups arranged round a fifth similar group, constituting a molecular nucleus.

The first action of hydrolysis by diastase is to break up this complex, and to liberate all the five amylin-groups. Four of these groups when liberated are capable, by successive hydrolysis through maltodextrans, of being rapidly and completely converted into maltose, whilst the central amylin nucleus, by a closing up of the molecule, withstands the influence of hydrolysing agents and constitutes the stable dextrin of the low equation, which, as we know, is so slowly acted upon by subsequent treatment with diastase. The four readily hydrolysable amylin-groups we look upon as of equal value, and in their original state these constitute the so-called high dextrans, which can never be separated completely from the low dextrin by any ordinary means of fractionation.

This hypothesis provides for intermediate maltodextrans or amylo-dextrans whose number is only limited by the size of the original amylin-group.

Each amylin-group of the five has a formula of  $(C_{12}H_{20}O_{10})_{20}$ , and a molecular weight of 6480; so that the entire starch-molecule, or more correctly speaking, that of soluble starch, is represented by  $5(C_{12}H_{20}O_{10})_{20}$ , having a molecular weight of 32,400.

An attentive consideration of all the facts which have been brought forward, both by ourselves and others, in connection with the transformation of starch by diastase, will, we think, show them to be in accordance with this view, and the hypothesis which we now advance

is sufficient to support those facts and to give some sort of explanation of them, whilst, at the same time, it may serve as a new starting point for further investigation.

*Appendix.*

The gradual diminution in the molecular weight of the products of hydrolysis of a mixture of the so-called high and low dextrans is well shown in the following experiment, in which a solution of the dextrans was treated with successive small quantities of diastase, and submitted from time to time to Raoult's method.

Correction has been made for the amounts of diastase, but the "coefficient of depression"  $A$  has, in each case, been calculated on the original amount of solid matter, thus neglecting the fixation of water which takes place as the hydrolysis proceeds.

11.1335 grams of substance in 93.28 grams water.

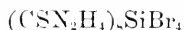
	E.	C.	A.	M.
Before addition of diastase . . . . .	+0.035	0.050 <sup>2</sup>	0.0043	4418
5 mins. after 1st addition of diastase	+0.000	0.060	0.0050	3800
15       "       "       "	-0.010	0.070	0.0058	3276
15 hours after 1st addition of diastase	-0.255	0.315	0.0263	722
16       "       "       "	-0.265	0.325	0.0272	698
1 hour after 2nd addition of diastase	-0.350	0.380	0.0318	597
1       "       3rd addition of diastase	-0.410	0.410	0.0343	554

XLVI.—*Researches on Silicon Compounds and their Derivatives.*

Part V. *On Silicotetraphenylamide, Para- and Ortho-silicotetratolylamides,  $\alpha$ - and  $\beta$ -Silicotetranaphthylantides.*

By J. EMERSON REYNOLDS, M.D., F.R.S., Professor of Chemistry,  
University of Dublin.

IN former communications I have shown that silicon tetrabromide can combine with several thiocarbamides without loss of halogen, and form highly condensed compounds of the type—



(Trans., 51, 203, and 53, 853).

I have now the pleasure to lay before the Society an account of certain interactions with amidic compounds in which silicon bromide and chloride lose all their halogen and afford a new class of silicon-derivatives. In the following pages I shall describe the preparation



and chief properties of five of these new substances, viz., silico-tetraphenylamide, para- and ortho-silicotetratolylamides,  $\alpha$ - and  $\beta$ -silicotetranaphthylamides.

*Silicotetraphenylamide.*

When silicon tetrabromide is added to excess of aniline diluted with 3 to 4 vols. of benzene, much heat is evolved, and aniline hydrobromide separates out, as it is nearly insoluble in benzene. If aniline be in excess throughout the operation, the whole of the halogen precipitates as aniline salt, and there remains in solution a beautiful crystallisable compound which is silicotetraphenylamide. If the aniline be not in excess throughout the operation, a bromo-compound appears to be produced analogous to Harden's (Trans., 51, 40) rather ill-defined chlorinated product.

Silicon tetrachloride acts in a similar manner with excess of aniline and, being less costly than the tetrabromide, can be advantageously used instead of the latter in comparatively large operations. The most convenient mode of preparing considerable quantities of the new compound with the aid of the chloride will appear from the following detailed account of an experiment.

A mixture of 100 grams of silicon tetrachloride with twice the volume of benzene was gradually added to 438 grams of pure aniline, also diluted with 2 vols. of benzene. Constant agitation was maintained during the addition of the chloride, and the latter was added more slowly towards the end of the operation. The product was quickly filtered from the separated aniline hydrochloride and the latter repeatedly washed with fresh benzene. The filtrate was then distilled as far as possible from a water-bath, and finally over a naked flame at 100—105°, in a current of dry hydrogen, to remove as much benzene as possible; a syrupy liquid was left after this treatment. Experience of former preparations indicated that, while the liquid would solidify to an obscurely crystalline mass after some days, it was better to pour it still warm into an excess of carbon bisulphide, with which the syrup mixed completely. After rapid filtration from a little aniline hydrochloride, which was separated by the bisulphide, the clear solution was slowly distilled at as low a temperature as possible until reduced to the crystallising point, and it was then set aside to cool. A fine crop of large, transparent, lustrous crystals of the new compound separated, and the mother-liquors from these afforded a further supply, so that rather more than 120 grams were obtained nearly free from secondary products, of which thiocarbanilide is the most troublesome. It was subsequently found that the yield could be considerably increased by the addition of light petroleum to

the mother-liquors, which precipitates small crystals of the tetramide from its solutions in carbon bisulphide or benzene. Two crystallisations of the best crops from fresh bisulphide yielded the new compound in a state of purity and in fine, colourless, transparent crystals, which are formed at the surface of the solution, as they are specifically lighter than the liquid. These crystals did not contain any trace of chlorine.

Products of different operations, which had been three times recrystallised from carbon bisulphide, were used in the following analyses:—

- I. 0.693 gram gave 0.103 of  $\text{SiO}_2$ . Si = 6.93 per cent.  
 II. 0.7505 gram gave 0.1115 of  $\text{SiO}_2$ . Si = 6.93 per cent.  
 III. 0.261 gram gave 32.8 c.c. of N at  $16^\circ$  and 751 mm. N = 14.45 per cent.  
 IV. 0.23 gram gave 27 c.c. of N at  $11^\circ$  and 766 mm. N = 14.03 per cent.  
 V. 0.2325 gram gave 0.138 of  $\text{H}_2\text{O}$  and 0.6185 of  $\text{CO}_2$ . H = 6.59 and C = 72.55 per cent.  
 VI. 0.2212 gram gave 0.127 of  $\text{H}_2\text{O}$  and 0.59 of  $\text{CO}_2$ . H = 6.37 and C = 72.73 per cent.

These results\* agree with the formula—



		Experiment.	
		I.	II.
Si .....	Calculated. 7.07	6.93	6.93
C .....	72.72	72.55	72.73
H .....	6.06	6.59	6.37
N .....	14.15	14.45	14.03

The reaction which ensues when the silicon haloïd is gradually added to excess of aniline is therefore represented by the following equation:—



which accords with the weight of hydrochloride separated in the reaction.

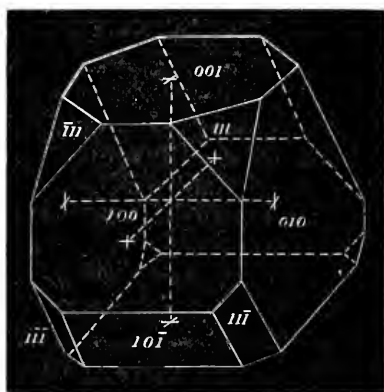
Silicotetraphenylamide when pure occurs in fine, colourless, transparent crystals, which have been subjected to crystallographic

\* It was observed that half the nitrogen came off readily from the compound when burned with lead chromate and copper oxide, but the residue very slowly, and at the end the temperature had to be raised as high as practicable in order to ensure complete combustion.

examination by my friend Professor Sollas, F.R.S., whom I have to thank for the following statement of his results:—

“Crystalline system, oblique (monoclinic);  $\beta = 110^\circ 20'$ ; ratio of parameters,  $a : b : c = 0.9853 : 1 : 1.043$ .

“The crystals consist of the following forms:—(100), (010) (111), (111), (101). The planes about the lower pole, with the exception of 001, are frequently reduced and sometimes completely suppressed,



hemimorphic crystals resulting: twins occasionally occur, with 001 as the plane of combination, and a normal to it as the twinning axis.

“The cleavage is highly perfect parallel to 001, perfect parallel to 010, scarcely perfect parallel to 100: traces of cleavage parallel to the pyramidal faces are obtainable.

“The plane of the optic axes lies in the plane of symmetry, and the acute bisectrix makes an angle of  $27^\circ 20'$  with the axis  $c$  in the obtuse angle  $\beta$ . The apparent angle with sodium light in air is  $31^\circ 5'$ , and in bromonaphthalene (r. i. = 1.66)  $18^\circ 36'$ . A parallel sided flake obtained by cleavage along the 001 plane almost completely loses visibility when immersed in methylene iodide (r. i. = 1.7446), the mean refractive index is therefore approximately 1.7446. The true angle between the optic axes is consequently  $17^\circ 40'$ .

“The dispersion is inclined,  $p$  slightly less than  $v$ . The double refraction is negative.

“The extinction angle measured on the 010 plane is  $7^\circ$ , the edge 010, 001 being taken for reference.”

The pure compound melts at  $137$ – $138^\circ$  to a nearly transparent liquid which can be heated in a narrow tube to  $210^\circ$  without decomposition.

Heated in a vacuum to its melting point, some aniline is given off,

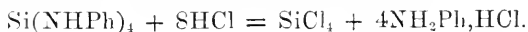
and a mixture of silicon compounds formed whose constituents will be described later on.

Silicotetraphenylamide is very soluble in benzene but less soluble in carbon bisulphide (100 c.c. of the solution saturated at 14° contain 21.1 grams). The compound is separated from both solutions on addition of light petroleum, in which it is almost insoluble, hence in recent preparations the latter has been used with advantage in separating the pure compound. It is at once decomposed by chloroform; anhydrous ether dissolves the compound without apparent decomposition, but alcohol and water decompose it; the latter very slowly yields silicic acid and aniline. Rapid decomposition takes place if either acids or alkalis are present, especially in alcoholic solution.

So far as silicotetraphenylamide has been hitherto examined, it has not shown any distinct tendency to unite as a whole with acids, but is rather decomposed by them, even when the amide is present in considerable excess. The nature of the decomposition which takes place with hydrochloric acid appears from the results of the following experiment.

Silicotetraphenylamide was dissolved in benzene and a current of dry hydrochloric acid gas was led through it. There was immediate separation of a white substance which increased as the current of gas continued. The mixture was ultimately saturated with hydrochloric acid gas and was allowed to stand for two days; it was then filtered, the precipitate washed with benzene, and dried for analysis, during which it slightly fumed. The filtrate was not precipitated on largely diluting it with light petroleum, proving that all the silicotetraphenylamide had been separated from it. On the other hand, it contained silicon chloride in comparatively large quantity.

The precipitate was found to contain 26.51 per cent. of chlorine, but only 0.79 per cent. of silicon. It was, therefore, chiefly aniline hydrochloride from which all traces of silicon tetrachloride had not been washed out. The action of hydrochloric acid on the silicon compound is therefore represented by the equation—



There was not any evidence that a hydrochloride of silicotetraphenylamide was formed at any period of the reaction. The insolubility of aniline hydrochloride in benzene doubtless facilitated the action of hydrochloric acid.

#### *Silicotetraparatolylamide.*

At an early stage of this investigation, it was found that para- and ortho-toluidines react with the silicon haloids in a manner similar to

aniline. As paratoluidine is most easily obtained in a state of purity, owing to the readiness with which it can be crystallised, I shall first state the results obtained with it.

To 254 grams of pure paratoluidine dissolved in benzene, 59 grams of silicon tetrachloride, also mixed with benzene, were added. An immediate separation of the hydrochloride took place, and when the whole of the reagents were mixed the hydrochloride was collected, washed with benzene, quickly dried and weighed. 170 grams of the imperfectly washed hydrochloride were obtained, whereas the following equation requires 168 grams:—



There is, therefore, practically complete separation of the hydrochloride, and nothing but the silicon compound could remain in solution. The latter had most of the benzene distilled from it, as in the case of the aniline compound; the residue was then mixed with carbon bisulphide which separated a very small quantity of hydrochloride, and the filtrate from this was then distilled down to a small bulk; on cooling it became semi-solid owing to the separation of botryoidal masses of crystals. The product was purified, with considerable loss, by pressure and recrystallisation from benzene, and was finally precipitated from its benzene solution by light petroleum and dried for analysis.

I. 0.859 gram gave 0.115 of  $\text{SiO}_2$ . Si = 6.24 per cent.

II. 0.6192 gram gave 0.081 of  $\text{SiO}_2$ . Si = 6.10 per cent.

III. 0.2315 gram gave 0.15 of  $\text{H}_2\text{O}$  and 0.6285 of  $\text{CO}_2$ . H = 7.17 and C = 74.04 per cent.

IV. 0.2374 gram gave 24 c.c. of N at  $12^\circ$  and 767 mm. N = 12.04 per cent.

V. 0.213 gram gave 21.15 c.c. of N at  $14^\circ$  and 771 mm. N = 12.15 per cent.

The results\* agree with the formula—



		Experiment.	
	Calculated.	I.	II.
Si .....	6.19	6.24	6.10
C .....	74.35	74.04	—
H .....	7.08	7.19	—
N .....	12.38	12.05	12.15

\* The combustions were made with mixtures of lead chromate and copper oxide. As in the case of silicotetraphenylamide, the temperature required at the end was high: moreover, in the nitrogen determinations, sensibly half the gas was quickly obtained, whilst the rest came off very slowly.

Silicoparatolylamide crystallises in small botryoïdal aggregations of fine needles which are colourless and transparent. They fuse at 131—132°, and decompose when more strongly heated, yielding paratoluidine. The compound is freely soluble in benzene, carbon bisulphide, and anhydrous ether, but is dissolved to a small extent only by light petroleum, which can, therefore, be used to precipitate it from its solution in the other liquids. It is decomposed by alcohol and water.

*Silicotetraorthotolylamide.*

In order to prepare this compound, 253 grams of pure redistilled orthotoluidine, mixed with twice its volume of benzene, was treated as in the former cases with silicon tetrachloride (50 grams) diluted with 4 vols. of benzene. Orthotoluidine hydrochloride did not begin to separate until about one-fifth of the silicon chloride had been added, as it is more soluble in benzene than the para-compound. After complete mixture of the reagents, the whole was allowed to stand over night and the hydrochloride then filtered off. The benzene was slowly distilled from the filtrate, and at the end the temperature was raised to 110°, while a current of dry hydrogen was passed over the residue to aid the removal of benzene. A thick, somewhat crystalline magma remained which was treated in the cold with carbon bisulphide. The bisulphide left 30 grams of orthotoluidine hydrochloride undissolved, which with 137 grams separated in the first treatment, gave a total quantity of 167 grams instead of the theoretical yield of 168 grams from the orthotoluidine taken, if the following equation expresses the change :—



The carbon bisulphide solution was concentrated by distillation, during which operation a further small quantity of hydrochloride separated and was removed. When heated on the water-bath until carbon bisulphide ceased to pass over, the residual liquid refused to crystallise on cooling. It was then exposed as a thin layer under the receiver of an air-pump which was frequently exhausted during 10 days, at the end of which time it gradually solidified to a crystalline mass.

In another preparation it has been found that the use of carbon bisulphide can be dispensed with, and the orthotoluidine hydrochloride can be completely removed from the benzene solution by addition of light petroleum. The silicon compound is not precipitated by light petroleum, unlike the para-derivative, and when the mixed benzene and light petroleum solution is distilled a very thick, syrupy

liquid remains, which after long exposure in a vacuum gradually yields a quantity of minute needles of the silicon compound.

When purified as completely as possible, by quick washing with light petroleum and by pressure, a specimen of the crystals gave the following analytical data :

- I. 1.6105 gram gave 0.2204 of  $\text{SiO}_2$ .  
 II. 0.3366 gram gave 35 c.c. N at  $18^\circ$  and 767.5 mm.

These results agree with the formula —



	Calculated.	Experiment.
Si . . . . .	6.19	6.38
N . . . . .	12.38	12.06

Silicotetraorthotolylamide forms small, colourless, transparent prisms, which do not readily form aggregations. They are very easily soluble in benzene, carbon bisulphide, and light petroleum, and consequently are difficult of complete purification. Water and alcohol decompose the compound.

#### *Silicotetranaphthylamides.*

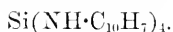
It was obviously desirable to ascertain whether double ring amidic compounds, such as the naphthylamines, interact with silicon haloids in a manner similar to those which include a single benzene nucleus. The following results prove that the two naphthylamines afford silicon-derivatives analogous to those obtained from aniline and the toluidines.

It was found that the  $\beta$ -naphthylamine derivative, like the paratoluidine product, was that most easily obtained in crystalline form; the  $\alpha$ -naphthylamine derivative being even less disposed to crystallise than that afforded by orthotoluidine.

*Silicotetrabetanaphthylamide* was produced on the addition of a benzene solution of 10 grams of silicon tetrachloride to 67.3 grams of pure  $\beta$ -naphthylamine also dissolved in benzene. After separation of the hydrochloride produced in the reaction, the concentrated benzene solution was treated as already described in the other cases, and then with light petroleum, when numerous small nodular masses of slightly coloured crystals separated. These were redissolved in benzene, again separated by petroleum, collected, washed, pressed, and dried for analysis.

- I. 0.461 gram gave 0.0439 of  $\text{SiO}_2$ .  
 II. 0.3542 gram gave 29.5 c.c. of N at  $18^\circ$  and 768.5 mm.

These results agree fairly with the formula—



	Calculated.	Experiment.
Si . . . . .	4.69	4.34
N . . . . .	9.39	9.60

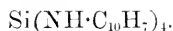
This compound in crystallising carries down with it some free naphthylamine which it is difficult to remove. The purest product obtained is very readily decomposed by heat, while it partially melts and assumes a brown colour. It is soluble in benzene and carbon bisulphide, but is only slightly soluble in light petroleum. Like other compounds of the kind it is readily decomposed by water.

*Silicotetraphenaphthylamide* was produced from  $\alpha$ -naphthylamine by similar treatment, but unlike the  $\beta$ -compound it was not separated from benzene on the addition of light petroleum. When the mixed petroleum and benzene solution was evaporated, a thick, brown oil separated, and this oil, after gentle heating in a current of dry hydrogen, slowly solidified to a mass of minute crystals.

The best product yielded the following numbers on analysis:—

- I. 0.6305 gram gave 0.061 of  $\text{SiO}_2$ . Si = 4.51 per cent.
- II. 0.2148 gram gave 16.7 c.c. of N at  $20^\circ$  and 766.5 mm.  
N = 8.92 per cent.

Although these results show that the material was still somewhat impure, the ratio of nitrogen to silicon is 4 : 1, or that required by the formula—



The  $\alpha$ -compound is acted on by solvents, heat, and water, even more readily than the substance afforded by  $\beta$ -naphthylamine, but, unlike the latter, is not separated in crystalline form by light petroleum.

I have to thank Mr. Emil A. Werner, F.C.S., for the assistance he has rendered in carrying out the work recorded in this paper

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XLVII.—*The Vapour-pressures of Quinoline.*

By SYDNEY YOUNG, D.Sc., Professor of Chemistry, University College, Bristol.

FOUR years ago Dr. Ramsay and I communicated to the Society (Trans., **47**, 640) the results of determinations of the vapour-pressures of chlorobenzene, bromobenzene, aniline, methyl salicylate, and bromonaphthalene, and in the following year (*ibid.*, **49**, 37) of mercury. We have constantly made use of these liquids, as well as of carbon bisulphide and ethyl alcohol, the vapour-pressures of which have been determined by Regnault, for obtaining constant known temperatures—the tube or vessel to be heated being placed in the vapour of the liquid boiling under known pressure. This method of heating possesses the two great advantages that the temperature can be kept constant for any length of time, or it can be altered by a definite amount in a very few minutes.

With the exception of methyl salicylate, these liquids have given excellent results, but the salicylic ether is open to several objections; it is not easy to obtain a product of constant boiling point; the ether is hygroscopic, and the moisture, besides being difficult to remove, causes slow hydrolysis, so that the liquid, after being used for some time, is always found to be contaminated with salicylic acid. Good results have, indeed, been obtained with methyl salicylate, but its employment has involved considerable loss of time owing to the necessity for frequent redistillation of the liquid, besides the preliminary very tedious fractionation. It appeared advisable, therefore, if possible, to substitute some other liquid less open to objection, and it occurred to me that quinoline might give good results. This substance is supplied by Kahlbaum in a pure state at a moderate price; although it is hygroscopic, the water has no action on the compound, and is rapidly expelled on distillation; lastly, the boiling point ( $237.5^{\circ}$ ) is not far from midway between those of aniline and bromonaphthalene. Determinations were made with two samples of quinoline, one (K) obtained from Kahlbaum, the other (H) from Messrs. Harrington Brothers of Cork; the second sample required fractionation, but was easily obtained pure, and identical results were obtained with both. In the course of distillation, the following determinations of boiling point were made:—

	Pressure.	Temperature observed.	Corrected to 760 mm.
K.....	749·2	236·9°	237·55°
H.....	750·4	237·0	237·55
H.....	751·6	237·0	237·5
K.....	758·3	237·4	237·5

Calculated from constants for Biot's formula . . . . 237·45°

These determinations agree fairly well with that of Skraup, 237·1° at 746·8 mm., or 237·8° at 760 mm. At low pressures the determinations were made with the apparatus described by Dr. Ramsay and myself; at higher pressures the thermometer was placed in the vapour of the liquid boiling under known pressures.

The temperatures are those of an air thermometer; the pressures are in millimetres of mercury at 0°. The thermometer was one of the two employed in my work on benzene and its halogen-derivatives (p. 489).

### *Experimental Results.*

#### Series I (K).

Pressure.	Temp.	Pressure.	Temp.	Pressure.	Temp.	Pressure.	Temp.
2·55	75·3°	9·3	102·1°	26·75	126·05°	70·0	152·15°
2·75	78·3	10·65	104·3	29·25	128·6	77·2	154·95
3·25	81·1	11·8	107·4	33·6	132·35	84·8	157·85
3·75	83·05	13·6	110·05	37·4	134·95	101·3	163·05
4·55	86·55	15·6	113·05	42·1	138·1	109·4	165·4
5·50	90·05	17·55	115·9	47·3	141·05	119·7	168·05
6·15	93·65	19·1	118·1	54·15	144·15	131·2	170·95
7·15	96·55	21·3	120·75	58·0	146·65	—	—
8·1	99·45	23·85	123·45	64·1	149·5	—	—

#### Series II (K).

101·7	162·3°	288·35	198·1°	428·45	213·2°	610·9	228·0°
115·65	166·85	313·95	201·2	460·0	216·05	656·0	231·1
232·55	190·1	339·35	204·1	493·0	218·9	701·7	233·95
249·5	192·65	368·1	207·2	528·8	221·9	745·3	236·65
269·2	195·55	395·8	210·1	568·3	224·95	—	—

#### Series III (H).

90·2	159·15°	159·8	177·35°	263·9	194·65°	500·0	219·35°
93·25	160·15	171·85	179·6	304·9	200·15	560·3	224·25
107·2	164·6	190·45	183·15	346·8	205·05	621·1	228·45
132·6	171·05	213·8	187·15	400·7	210·2	683·3	232·8
147·55	174·5	233·2	190·2	448·2	214·8	745·3	236·55

The logarithms of these pressures were mapped against temperature, and the logarithms of pressures corresponding to even temperatures read off. Constants for Biot's formula ( $\log p = a + bx' + c\beta'$ ) were then calculated, and from these constants the pressures corresponding to definite temperatures—each  $10^\circ$  from  $80^\circ$  to  $180^\circ$  and each degree from  $180^\circ$  to  $240^\circ$ —were recalculated.

The constants for Biot's formula are—

$$\begin{aligned} a &= 0.787142 \\ b &= 2.510713 & \log b &= 0.3997970 \\ c &= -2.806455 & \log c &= 0.4481581 \\ \log \alpha &= 0.00047375 & \log \beta &= 1.99682426 \\ t &= t^\circ \text{C} - 80. \end{aligned}$$

The calculated pressures are given in the following tables:—

# I.

Temp.	Pressure.	Temp.	Pressure.	Temp.	Pressure.	Temp.	Pressure.
80°	3.10	130°	31.02	180°	172.4	230°	641.3
90	5.21	140	45.49	190	230.4	240	801.6
100	8.48	150	65.31	200	303.4	—	—
110	13.42	160	91.90	210	394.2	—	—
120	20.66	170	126.9	220	505.7	—	—

# II.

180°	172.4	196°	272.2	212°	414.7	228°	612.1
181	177.6	197	279.7	213	425.3	229	626.6
182	182.9	198	287.4	214	436.1	230	641.3
183	188.3	199	295.3	215	447.1	231	656.3
184	193.9	200	303.4	216	458.4	232	671.6
185	199.6	201	311.6	217	469.9	233	687.2
186	205.5	202	320.0	218	481.6	234	703.1
187	211.5	203	328.6	219	493.5	235	719.3
188	217.6	204	333.7	220	505.7	236	735.7
189	223.9	205	346.4	221	518.1	237	752.5
190	230.4	206	355.5	222	530.8	238	769.5
191	237.0	207	364.9	223	543.7	239	786.9
192	243.7	208	374.5	224	556.9	240	804.6
193	250.6	209	384.2	225	570.3	—	—
194	257.6	210	394.2	226	584.0	—	—
195	264.8	211	404.3	227	597.9	—	—

XLVIII.—*On the Vapour-pressures and Specific Volumes of Similar Compounds of Elements in relation to the Position of those Elements in the Periodic Table.* Part I.

By SYDNEY YOUNG, D.Sc., Professor of Chemistry, University College, Bristol.

AT the meeting of the British Association held in Aberdeen in 1885, it was pointed out, in a paper published jointly by Dr. Ramsay and myself, (1) that when different substances are compared at temperatures at which their vapour-pressures are equal, the product  $dp/dt \cdot T$  (where  $T$  is the absolute temperature) is approximately a constant, and that for nearly related compounds, such as ethyl chloride and ethyl bromide, or chlorobenzene and bromobenzene, the products appear to be really equal; (2) that if these values of  $dp/dt \cdot T$  are compared at a series of equal pressures, their ratios to each other remain approximately unchanged with alteration of pressure, and that for nearly related bodies they remain identical at all pressures for which data are available. If the values of  $dp/dt \cdot T$  for any two compounds are identical throughout the series of equal pressures, it follows that the ratios of the absolute temperatures themselves must be also constant at equal pressures; in other words, the ratio of the boiling points, expressed in absolute temperatures, must be constant whatever the pressure. In the majority of cases, however, in which the values of  $dp/dt \cdot T$  are only approximately equal at equal pressures, and where the ratios of these values to each other do not remain quite unchanged with alteration of pressure, the ratios of the boiling points cannot be quite constant at all equal pressures. It was found, however, that for a range of pressure at any rate from about 100 to 3000 or 5000 mm., the relation expressed by the equation  $R' = R + c(t' - t)$  is applicable to any two substances, whether nearly related or not.

$R'$  is the ratio of the absolute temperatures at a pressure  $p'$ ,  $R$  the ratio at  $p$ ;  $t'$  and  $t$  are the temperatures of one of the two substances corresponding to the two pressures  $p'$  and  $p$ ;  $c$  is a constant, which for nearly related bodies = 0, when  $R' = R$ .

These and other generalisations are fully described in the *Phil. Mag.* (Dec., 1885, and Jan., 1886).

I am at present engaged in a study of the vapour-pressures and specific volumes of the halogen-compounds of a number of elements, in order to find whether the ratios of the boiling points (in absolute temperatures) of similar compounds of elements which belong to the

same group in the periodic table are constant at all equal pressures, and whether any such simple relation holds good for the specific volumes. But before doing this it seemed desirable to compare the halogens among themselves, and for this purpose the mono-substitution products of benzene were chosen, as they are all stable substances, and can be obtained in a state of purity. At the same time, the vapour-pressures and specific volumes of benzene itself were determined, in order to ascertain the effect of substituting an atom of hydrogen for an atom of a halogen.

The present paper contains details of determinations of the vapour-pressures and specific volumes of benzene, fluorbenzene, chlorobenzene, bromobenzene, and iodobenzene within the widest attainable limits of temperature and pressure, followed by an account of the deductions drawn from the data obtained.

*Preparation of the Pure Substances. Benzene.*—A sample of carefully purified benzene, prepared by Dr. Ramsay and myself for our determinations of the vapour-pressures of solid and liquid benzene at low temperatures, was employed (*Phil. Mag.*, 1887, 61).

*Fluorbenzene.*—This compound was prepared, as described by Wallach (*Annalen* 235, 255), also Wallach and Hensler (*ibid.*, 243, 219), by the action of concentrated hydrofluoric acid on benzenediazopiperidide,  $C_6H_5 \cdot N \cdot N \cdot N \cdot C_5H_9$ . After fractionation, rather more than 50 grams of the pure product was obtained; it boiled with perfect constancy.

Substance.	Pressure in mm. reduced to 0°.	Boiling point.	Boiling point under 760 mm. pressure.	
			From observed b. p.	Calculated from Biot's formula.
Benzene* . . . . .	753·4	79·9	80·2	80·25
Fluorbenzene† . . . .	764·2	85·3	85·1	85·2
	769·0	85·6	85·2	—
	730·4	83·85	85·15	—
Chlorobenzene‡ . . . .	—	—	—	132·0
Bromobenzene‡ . . . .	—	—	—	156·0
Iodobenzene . . . . .	744·1	187·55	188·45	188·45
	746·3	187·65	188·4	—
	752·3	188·05	188·5	—
	756·4	188·2	188·4	—
	758·1	188·35	188·45	—

\* Ramsay and Young (*loc. cit.*).

† Wallach and Hensler (*loc. cit.*), 85°; Paternò and Oliveri (*Trans. Chem. Soc.*, 46, 426), 85–86°.

‡ Chlorobenzene and bromobenzene were used for the calibration of the thermometers (Ramsay and Young, *Trans. Chem. Soc.*, 1885, 47, 640).

*Chlorobenzene, Bromobenzene, Iodobenzene.*—These substances were obtained from Kahlbaum; they were repeatedly fractionated until products were obtained with perfectly constant boiling points.

The table (p. 487) gives the boiling points of these substances as actually observed under atmospheric pressure, and also reduced to 760 mm. pressure. As determinations by other observers are given in Carnelley's tables, it seems unnecessary to reproduce them here.

*Specific Gravities and Specific Volumes.*

The specific gravities (masses of 1 c.c.) were in each case determined in a Sprengel tube of the form recommended by Perkin; the weighings were reduced to a vacuum. The liquids were always redistilled immediately before the determinations, which were carried out first at 0° and then at about the atmospheric temperature, the Sprengel tube being placed in cold water of constant temperature.

Substance.	Temperature.	Specific gravity or mass of 1 c.c.	Specific volume or volume of 1 gram.
Benzene .....	0°	0·90006	1·11104
„ .....	18	0·88118	1·13484
Fluorobenzene .....	0	1·04653	0·95554
„ .....	12·86°	1·03149	0·96947
Chlorobenzene .....	0°	1·12786	0·88664
„ .....	0	1·12787*	—
„ .....	16·0°	1·11093	0·90015
Bromobenzene .....	0°	1·52182	0·65711
„ .....	14·55°	1·50242	0·66559
Iodobenzene .....	0°	1·86059	0·53746
„ .....	15·21°	1·83798	0·54407

The results of determinations by other observers are given in Clarke's "Constants of Nature," Part I, but it is unfortunately not stated in any case whether the specific gravities are compared with water at 4°, at 0°, or at the same temperature as the substance. As the error at 0° must be inconsiderable whether the water were taken at 0° or 4°, I give the results at this temperature for the sake of comparison.

\* Second determination some months later.

Substance.	Observer.	Reference.	Sp. gr. at 0°.
Benzene .....	Warren .....	<i>Jahresb.</i> , 18, 515 .....	0·8957
" .....	Kopp .....	<i>Pogg. Ann.</i> , 72, 243 .....	0·89911
" .....	Louguine .....	<i>Ann. Chim. Phys.</i> (4), 11, 453 .....	0·8995
" .....	Pisati and Paternò ..	<i>Trans. Chem. Soc.</i> , 27, 686 .....	0·89949
" .....	Adrieenz .....	<i>Berichte</i> , 6, 442 .....	0·90023
" .....	Dieff .....	<i>J. pr. Chem.</i> (2), 27, 368 .....	0·9000
Fluorbenzene ..	Wallach .....	<i>Annalen</i> , 235, 255 .....	1·024 (at 20°)*
" .....	Wallach and Heusler ..	" 243, 221 .....	1·0236 (at 20°)*
Chlorobenzene ..	Jungfleisch .....	<i>Jahresb.</i> , 21, 343 .....	1·1293
" .....	Adrieenz .....	<i>Berichte</i> , 6, 443 .....	1·12855
" .....	" .....	" .....	1·12818
Bromobenzene ..	Ladenburg .....	<i>Berichte</i> , 7, 1685 .....	1·519
" .....	" .....	" .....	1·522
" .....	Adrieenz .....	" 6, 444 .....	1·51768
" .....	Weger .....	<i>Annalen</i> , 221, 61 .....	1·5203
Iodobenzene ...	Schiff .....	<i>Beiblätter</i> , 9, 559 .....	1·8578

*Vapour-pressures below 760 mm.*

These were for the most part determined by means of the apparatus described by Dr. Ramsay and myself (*Trans.*, 1885, 47, 43), but two vertical tubes were connected with the condenser so as to admit of two temperature readings being taken at each pressure. The numbers given are not unfrequently the means of several pressure and temperature readings taken within very narrow limits. The thermometers contained air and were heated for 10 days to about 285° before calibration. In order to calibrate them, they were placed in melting ice and in the vapours of pure liquids boiling under known pressures; the zero points were redetermined from time to time, but were found to remain very nearly constant.

In the case of iodobenzene, for pressures above 250 mm., it was found better to boil the liquid in a bulb fused to a wide, vertical tube connected with a gauge and pump, and to place the thermometers in the vapour of the boiling liquid.

The vapour-pressures of benzene have been already determined by Dr. Ramsay and myself from the lowest pressures to 760 mm., and those of chlorobenzene and bromobenzene from moderately low pressures to the atmospheric pressure. It was, therefore, necessary to determine the vapour-pressures of chlorobenzene and bromobenzene

\* From the curve drawn from my determinations of the molecular volumes of fluorobenzene the specific gravity at 20° would be 1·0225; the value 1·0236 by Wallach and Heusler is given in terms of water at 4°.

TABLE I.—*Fluorbenzene.*

Pressure.	Temp.	Pressure.	Temp.	Pressure.	Temp.	Pressure.	Temp.
6.95	-17.85°	29.4	6.05°	111.3	33.3°	359.2	62.75°
8.15	-15.1	30.2	6.65	125.7	36.05	364.0	63.25
9.7	-13.0	31.3	7.3	143.4	39.15	398.7	65.65
10.85	-11.35	35.2	9.5	161.7	42.05	437.0	68.25
12.0	-9.45	37.5	10.65	187.5	45.55	480.0	71.0
13.0	-8.05	44.45	13.85	219.9	49.6	522.5	73.7
14.85	-5.95	51.55	16.75	222.8	49.9	563.05	75.9
16.05	-4.55	59.0	19.5	197.2	46.9	588.4	77.3
17.8	-3.0	66.25	22.0	201.6	47.6	613.1	78.6
19.95	-0.95	76.85	24.9	206.25	48.1	618.6	78.75
21.05	+0.15	86.45	27.5	246.75	52.6	624.1	79.15
23.1	1.8	99.0	30.6	248.9	52.95	633.2	79.55
24.1	2.6	—	—	282.1	56.2	659.8	80.7
26.1	4.1	89.05	28.25	283.8	56.4	694.2	82.45
27.1	4.7	97.5	30.35	320.2	59.6	730.4	83.85

*Chlorobenzene.*

3.15	2.95°	11.45	24.75°	16.9	31.85°	58.5	57.25°
5.05	10.15	12.5	26.45	18.1	33.0	61.45	58.65
5.35	11.55	13.15	27.3	20.75	35.45	78.1	64.2
6.4	15.1	14.35	28.7	24.8	38.95	79.1	64.55
8.45	19.6	14.8	29.25	35.3	46.25	111.5	73.05
10.5	23.25	15.8	30.3	36.4	47.0	170.85	84.2

*Bromobenzene.*

4.9	27.2°	13.65	45.9°	46.0	71.4°	81.7	85.2°
5.15	28.4	16.8	49.8	46.95	71.7	104.35	91.7
5.7	30.2	20.65	54.15	47.6	72.0	133.6	99.15
6.1	31.15	25.15	58.25	59.05	77.3	—	—
8.1	36.2	30.9	62.55	59.85	77.65	—	—
10.1	40.35	37.5	67.2	79.3	84.45	—	—

*Iodobenzene.*

1.6	29.3°	32.0	88.75°	107.9	120.65°	202.4	139.7°
1.8	33.0	36.15	91.55	168.7	120.9	231.85	144.0
2.75	40.1	41.0	94.75	123.5	124.65	261.75	148.15
3.85	46.3	—	—	154.2	130.5	302.3	153.1
5.65	52.5	30.2	87.45	176.45	135.95	336.3	156.8
7.0	57.0	36.15	91.6	182.05	136.7	370.55	160.2
8.9	61.45	50.15	100.35	214.2	142.0	404.2	163.5
10.4	64.5	50.7	100.5	256.3	147.65	442.6	166.8
12.2	67.8	51.9	101.4	260.95	148.25	489.6	170.65
14.45	70.9	62.4	105.65	—	—	532.9	173.8
17.0	74.45	71.75	109.5	121.15	123.9	581.4	177.35
20.25	78.4	83.1	113.4	134.0	126.85	639.4	181.2
23.75	81.9	94.8	116.95	154.7	131.2	683.2	184.0
27.55	85.5	96.3	117.35	177.95	135.5	756.4	188.2



only at the lowest temperatures, but those of fluorobenzene and iodobenzene through the whole range of temperature.

The results obtained are given in the table (p. 490).

The logarithms of the pressures were mapped against the temperatures, and the logarithms of the pressures corresponding to equal intervals of temperature read off. The corresponding pressures are given in Table III, p. 501.

#### *Constants at High Temperatures.*

The apparatus is similar in principle to that employed by Dr. Ramsay and myself (*Phil. Trans.*, **178**, A, 59) in our joint researches; it is, however, larger, and is modified in certain details.

The corrections for pressure were the same as those previously adopted (Ramsay and Young, *Phil. Trans.*, 1886, Part I, 124), but in addition the length of the comparatively short heated column of mercury was reduced to 0°; this correction is of very slight importance in the case of volatile substances such as those previously studied, but becomes considerable—relatively to the vapour-pressure—with high boiling substances, such as bromobenzene and iodobenzene. The vapour-pressure of mercury was not subtracted from the read pressures, for the liquid was always condensed completely immediately before taking readings of vapour-pressure, and the mercury vapour could not possibly make its way to any appreciable extent through the long column of liquid above it during the short time required for taking readings. Even with a gas above the mercury in these long, narrow tubes, the mercury vapour does not attain its full pressure for some hours, and with a liquid the progress of the vapour would be retarded to a very much greater extent.

The temperatures are in all cases those of an air thermometer, and the pressures, since they are corrected for deviation of air from Boyle's law, are expressed in true millimetres of mercury at 0°.

In most cases, two series of determinations of vapour-pressure were made, the first with a large quantity of liquid, the second with about one-tenth of the amount, and in both series readings of pressure were taken at several different volumes; it will be seen that the two series give concordant results—a proof of the purity of the liquids.

The results obtained are given in the following tables; the means of all pressures at each temperature are given in Table III.

TABLE II.—*Benzene.*

Temp.	Pressure.	Mean.	Temp.	Pressure.	Mean.
90°	1008 } 1007 } 1009 } 1008 } 1010 }	1008	170°	6389 } 6390 } 6386 } 6378 } 6386 }	6386
100°	1336 } 1334 } 1335 } 1335 } 1337 }	1335	180°	7635 } 7634 } 7632 } 7626 } 7625 }	7630
110°	1739 } 1739 } 1739 } 1738 } 1740 }	1739	180°	7608 } 7599 } 7599 } 7601 } 7613 }	7604
120°	2229 } 2231 } 2230 } 2229 } 2231 }	2230	190°	9043 } 9049 } 9049 } 9042 } 9043 }	9045
130°	2814 } 2814 } 2816 } 2815 } 2815 }	2815	200°	10651 } 10651 } 10649 } 10648 } 10649 }	10650
140°	3522 } 3519 } 3521 } 3518 } 3519 }	3520	210°	12455 } 12448 } 12460 } 12451 } 12452 }	12453
150°	4332 } 4330 } 4334 } 4332 } 4331 }	4332	220°	14493 } 14496 } 14490 } 14493 } 14491 }	14493
150°	4336 } 4340 } 4335 } 4335 } 4342 }	4338	230°	16834 } 16821 } 16822 } 16826 } 16824 }	16825
160°	5305 } 5297 } 5290 } 5295 } 5311 }	5300	240°	19361 } 19359 } 19349 } 16345 } 19346 }	19352

*Benzene (continued).*

Temp.	Pressure.	Mean.	Temp.	Pressure.	Mean.
250°	22181 } 22199 } 22181 } 22161 } 22190 }	22182	280°	32801 } 32757 } 32774 } 32789 } 32789 }	32782
260°	25339 } 25326 } 25309 } 25320 } 25349 }	25329	284.3 — 286.1 — 288.0 — 288.5 — { Critical point	— — — — —	34594 35436 36226 36395 }
270°	28858 } 28840 } 28842 } 28861 } 28858 }	28852			

*Fluorbenzene.—I.*

90°	883 } 883 } 882 } 883 } 882 }	882.5	130°	2533 } 2534 } 2536 } 2537 } 2537 }	2535
100°	1178 } 1176 } 1177 } 1177 } 1177 }	1177	140	3171 } 3172 } 3173 } 3172 } 3172 }	3172
110°	1542 } 1542 } 1542 } 1541 } 1543 }	1542	150°	3928 } 3926 } 3922 } 3929 } 3927 }	3926
120°	1989 } 1989 } 1989 } 1989 } 1990 }	1989	150°	3937 } 3932 } 3931 } 3929 } 3929 }	3932
130°	2524 } 2524 } 2523 } 2525 } 2524 }	2524	160°	4831 } 4836 } 4828 } 4824 } 4825 }	4829

*Fluorbenzene.—I (continued).*

Temp.	Pressure.	Mean.	Temp.	Pressure.	Mean.
170°	5848 } 5845 } 5836 } 5839 } 5839 }	5841	220°	13566 } 13564 } 13550 } 13552 }	13558
180°	7000 } 6998 } 7002 } 6996 }	6999	230°	15765 } 15725 } 15726 }	15739
180°	7001 } 7004 } 7014 } 7022 }	7013	240°	18160 } 18171 } 18181 }	18171
190°	8369 } 8373 } 8379 } 8385 }	8376	250°	20934 } 20906 } 20904 }	20915
200°	9904 } 9899 } 9898 } 9895 }	9899	260°	23948 } 23957 } 23964 }	23956
210°	11625 } 11613 } 11616 } 11615 }	11617	270°	27355 } 27350 } 27362 }	27356
220°	13559 } 13562 } 13549 } 13553 }	13556	275°	—	29200
			279·95	—	31204

*Series II.*

220°	13545 } 13532 } 13535 } 13538 } 13529 }	13536	240°	18153 } 18154 } 18143 } 18147 } 18158 }	18151
230°	15729 } 15708 } 15703 } 15704 } 15703 }	15709	250°	20912 } 20891 } 20893 } 20889 } 20895 }	20896

*Fluorbenzene.—Series II (continued).*

Temp.	Pressure.	Mean.	Temp.	Pressure.	Mean.
260°	24005 } 23963 } 23962 } 23939 } 23952 }	23964	280·6°	31462 } 31432 } 31458 } 31470 }	31455
270°	27390 } 27371 } 27365 } 27375 } 27348 }	27370	283·3° 285·7 { 286·55 Critical	— — — point	32569 33608 33912 }

*Chlorobenzene.—I.*

150°	1211 } 1213 } 1215 }	1213	220°	5033 } 5042 } 5043 }	5039
160°	1538 } 1539 } 1541 }	1539	220°	5071 } 5064 } 5062 }	5066
170°	1920 } 1922 } 1923 }	1922	230°	6002 } 5988 } 5994 }	5995
180°	2370 } 2274 } 2376 }	2373	240°	7057 } 7065 } 7078 }	7067
180°	2371 } 2377 } 2377 }	2375	250°	8255 } 8262 } 8281 }	8266
190°	2907 } 2908 } 2913 }	2909	260°	9612 } 9633 } 9655 }	9633
200°	3526 } 3535 } 3539 }	3533	270°	11163 } 11163 } 11182 }	11169
210·7	4279 } 4281 } 4285 }	4282			

*Series II.*

Temp.	Pressure.	Mean.	Temp.	Pressure.	Mean.
140°	939 } 939 } 939 } 940 } 940 }	939.5	210°	4231 } 4227 } 4231 } 4228 } 4228 }	4229
150°	1205 } 1203 } 1204 } 1204 } 1205 }	1204	220°	5051 } 5054 } 5049 } 5042 } 5044 }	5048
150°	1208 } 1207 } 1208 } 1207 } 1206 }	1207	220°	5064 } 5056 } 5065 } 5062 } 5064 }	5062
160°	1532 } 1533 } 1533 } 1534 } 1534 }	1533	230°	5986 } 5992 } 5979 } 5986 } 5989 }	5986
170°	1921 } 1921 } 1919 } 1917 } 1918 }	1919	240°	7047 } 7049 } 7062 } 7050 } 7048 }	7051
180°	2373 } 2368 } 2370 } 2370 } 2367 }	2370	250°	8265 } 8271 } 8273 } 8265 } 8251 }	8265
180°	2369 } 2370 } 2370 } 2370 } 2371 }	2370	250°	8278 } 8270 } 8277 } 8276 } 8276 }	8275
190°	2903 } 2899 } 2901 } 2899 } 2902 }	2901	260°	9661 } 9660 } 9646 } 9643 } 9643 }	9648
200°	3520 } 3521 } 3522 } 3521 } 3521 }	3521	270°	11199 } 11196 } 11198 } 11186 } 11187 }	11192

A few determinations at higher temperatures are given later on.

*Bromobenzene.—I.*

Temp.	Pressure.	Mean.	Temp.	Pressure.	Mean.
170°	1077 } 1079 } 1079 } 1080 }	1079	220°	3050 } 3049 } 3054 }	3051
180°	1348 } 1349 } 1351 } 1352 }	1350	220°	3051 } 3051 } 3060 }	3054
180°	1358 } 1361 }	1359	230°	3646 } 3655 } 3669 }	3657
190°	1681 } 1681 } 1682 } 1684 }	1682	240°	4354 } 4358 } 4364 }	4359
200°	2074 } 2075 } 2077 } 2082 }	2077	250°	5152 } 5154 } 5157 }	5154
210°	2519 } 2520 } 2519 } 2526 }	2521	260°	6056 } 6056 } 6074 }	6062

*Series II.*

160°	846 } 846 } 846 } 846 }	846	180°	1354 } 1356 } 1357 } 1357 } 1358 }	1356
170°	1071 } 1073 } 1073 } 1075 } 1076 }	1074	190°	1684 } 1684 } 1685 } 1684 } 1685 }	1684
180°	1347 } 1348 } 1347 } 1349 } 1348 }	1348	200°	2076 } 2076 } 2076 } 2073 } 2074 }	2075

*Bromobenzene.—Series II (continued).*

Temp.	Pressure.	Mean.	Temp.	Pressure.	Mean.
210°	2532 } 2530 } 2529 } 2528 } 2528 }	2529	240°	4366 } 4363 } 4359 } 4353 }	4360
220°	3058 } 3054 } 3058 } 3057 } 3056 }	3057	250°	5159 } 5160 } 5160 } 5160 }	5160
220°	3056 } 3049 } 3048 } 3048 }	3050	260°	6096 } 6098 } 6089 } 6077 }	6090
230°	3662 } 3660 } 3659 } 3657 }	3659	270°	7118 } 7106 } 7108 } 7096 } 7096 }	7105

*Iodobenzene.—I.*

200°	991 } 990 } 991 } 991 }	991	230°	1853 } 1853 } 1857 }	1854
210°	1233 } 1230 } 1234 } 1233 }	1232	240°	2245 } 2246 } 2243 }	2245
220°	1516 } 1517 } 1519 } 1520 }	1518	250°	2702 } 2699 } 2699 }	2700
220°	1520 } 1522 } 1518 }	1520	260°	3222 } 3222 } 3219 }	3221
220°	1520 } 1522 } 1518 }	1520	270°	3821 } 3821 } 3819 }	3820



*Series II.*

Temp.	Pressure.	Mean.	Temp.	Pressure.	Mean.
220°	1521	1521	250°	2701	2700
	1521			2703	
	1523			2701	
	1522			2699	
	1520			2694	
230°	1852	1854	260°	3216	3216
	1853			3217	
	1856			3217	
	1856			3214	
	1854			3214	
240°	2246	2247	270°	3812	3810
	2245			3812	
	2251			3810	
	2248			3810	
	2244			3808	

Iodobenzene undergoes slow decomposition, shown by the gradual coloration of the liquid, when exposed to light at the ordinary temperature. At higher temperatures this is much more rapid, and it is also to be observed with bromobenzene, at any rate in contact with mercury. In the experiments with these substances at high temperatures, the tube was therefore carefully shielded from the light, and the decomposition was thus prevented in the case of bromobenzene, and was reduced to a very small amount with iodobenzene; but it was evidently not entirely prevented, for, after being heated to 270°, the liquid when cold contained a few fine, needle-shaped crystals.

In calculating the mean pressures from the results of the two series, greater weight has been given, in the case of chlorobenzene and of bromobenzene, to the second series, as the results are in all probability rather more accurate.

From the mean pressures at high temperatures and the pressures read from the curves at low temperatures, the constants for Biot's formula,  $\log p = a + bz^t + c\beta^t$ , were calculated.

These constants are—

*Benzene.*

$$a = -8.518142.$$

$$b = 12.126708$$

$$\log b = 1.0837430$$

$$c = -2.184666$$

$$\log c = 0.3393850$$

$$\log \alpha = 0.0001302029$$

$$\log \beta = 1.99589589$$

$$t = t^\circ \text{C.}$$

*Fluorbenzene.*

$$a = 3.193520.$$

$$\begin{array}{ll} b = 0.850980 & \log b = \bar{1}.9299191 \\ c = -2.723934 & \log c = 0.4351967 \\ \log \alpha = 0.000942654 & \log \beta = \bar{1}.99636976 \\ & t = t^{\circ} \text{C.} \end{array}$$

*Chlorobenzene.*

$$a = 2.392256.$$

$$\begin{array}{ll} b = 1.317190 & \log b = 0.1196485 \\ c = -2.523336 & \log c = 0.4019752 \\ \log \alpha = 0.00075845 & \log \beta = \bar{1}.99640773 \\ & t = t^{\circ} \text{C} - 30. \end{array}$$

*Bromobenzene.*

$$a = 6.481438.$$

$$\begin{array}{ll} b = -4.284691 & \log b = 0.6319196 \\ c = -1.443167 & \log c = 0.1593166 \\ \log \alpha = \bar{1}.99904908 & \log \beta = \bar{1}.99510535 \\ & t = t^{\circ} \text{C} - 30. \end{array}$$

*Iodobenzene.*

$$a = 3.253593.$$

$$\begin{array}{ll} b = 0.412170 & \log b = \bar{1}.6150762 \\ c = -3.501503 & \log c = 0.5442545 \\ \log \alpha = 0.001421982 & \log \beta = \bar{1}.99675426 \\ & t = t^{\circ} \text{C} - 30. \end{array}$$

The following table contains the observed and calculated vapour-pressures of the five liquids at definite temperatures. The pressures below 760 mm. are by the dynamical method, the higher ones by the statical; those included in a bracket are taken from previous papers by Dr. Ramsay and myself.

TABLE III.—Benzene.

Temp.	Pressure.		Difference.	Regnault.	Temp.	Pressure.		Difference.	Regnault.
	Observed.	Calculated.				Observed.	Calculated.		
-10°	14.97	14.83	-0.14	*12.92	140°	3520	3520.0	0.0	3520.7
0	26.54	26.54	0.00	*25.81	150	4335	4334.8	-0.2	4333.7
10	45.19	45.43	+0.24	45.25	160	5300	5281.9	-18.1	5271.4
20	74.13	74.66	0.53	75.05	170	6386	6374.1	-11.9	6340.7
30	117.45	118.24	0.79	120.24	180	7617	7625.2	+8.2	—
40	180.20	181.08	0.88	183.62	190	9045	9049.4	4.4	—
50	268.30	268.97	0.67	271.37	200	10650	10663.0	13.0	—
60	388.51	388.58	0.07	390.10	210	12453	12482.0	29.0	—
70	548.16	547.40	-0.76	547.42	220	14321	14526.0	5.0	—
80	755.0	753.62	-1.38	751.86	230	16825	16815.0	-10.0	—
90	1008.0	1016.1	+8.1	1012.75	240	19352	19369.0	+17.0	—
100	1335.0	1344.3	9.3	1340.05	250	22182	22214.0	32.0	—
110	1739.0	1748.2	9.2	1744.12	260	35329	25376.0	47.0	—
120	2230.0	2238.1	8.1	2235.44	270	28852	28855.0	33.0	—
130	2821.0	2824.9	3.9	2821.35	280	32782	32772.0	-10.0	—

\* Solid benzene.

*Fluorbenzene.*

Temp.	Pressure.			Temp.	Pressure.		
	Observed.	Calculated.	Diff.		Observed.	Calculated.	Diff.
-20°	6.15	6.15	0.00	110°	3172	3173.0	+1.0
-10	11.55	11.61	+0.06	150	3929	3931.4	2.4
0	20.92	20.92	0.00	160	4829	4816.7	-12.3
10	36.40	36.11	-0.29	170	5811	5841.6	+0.6
20	60.54	59.93	-0.61	180	7006	7018.9	12.9
30	96.61	95.94	-0.67	190	8376	8363.5	-12.5
40	149.6	148.56	-1.04	200	9899	9890.5	-8.5
50	223.9	223.16	-0.74	210	11617	11617.0	0.0
60	325.1	326.02	+0.92	220	13550	13561.0	+11.0
70	463.5	464.30	0.8	230	15724	15745.0	21.0
80	644.9	645.98	1.08	240	18161	18190.0	29.0
90	883.0	879.73	-3.27	250	20906	20921.0	18.0
100	1177.0	1174.9	-2.1	260	23960	23977.0	17.0
110	1542.0	1541.3	-0.7	270	27363	27384.0	21.0
120	1989.0	1989.2	+0.2	280	31217*	31182.0	-35.0
130	2530.0	2529.5	-0.5	—	—	—	—

\* Calculated from pressures observed at 279.95° and 280.6°.

*Chlorobenzene.*

	2.52	2.56	+0.04	150°	1206	1206.0	0.00
10	4.86	4.86	0.00	160	1534	1528.3	-5.7
20	8.76	8.83	0.07	170	1920	1912.8	-7.2
30	15.45	15.35	-0.10	180	2370	2367.2	-2.8
40	26.00	25.68	-0.32	190	2902	2899.4	-2.6
50	41.98	41.46	-0.52	200	3521	3518.3	-2.7
60	65.54	64.78	-0.76	210	4229	4233.0	+4.0
70	97.9	98.22	+0.32	220	5056	5053.8	-2.2
80	144.75	144.88	0.13	230	5989	5991.8	+2.8
90	208.35	208.35	0.00	240	7018	7059.6	11.6
100	292.75	292.76	0.01	250	8270	8270.5	0.5
110	402.55	402.72	0.17	260	9647	9639.8	-7.2
120	542.8	543.31	0.51	270	11188	11185.0	-3.0
130	718.95	720.03	1.08	280	—	12925.0	—
140	939.4	938.84	-0.56	—	—	—	—

*Bromobenzene.*

Temp.	Pressure.			Temp.	Observed.	Calculated.	Diff.
	Observed.	Calculated.	Diff.				
30°	5.67	5.67	0.00	160°	846	840.81	-5.19
40	9.99	10.00	+0.01	170	1077	1071.6	-5.4
50	16.96	16.92	-0.04	180	1351	1349.3	-1.7
60	27.61	27.54	-0.07	190	1684	1379.9	-4.1
70	43.55	43.31	-0.24	200	2075	2070.1	-4.9
80	66.22	66.01	-0.21	210	2527	2527.0	0.0
90	97.72	97.80	+0.08	220	3055	3057.8	+2.8
100	141.1	141.23	0.13	230	3659	3670.2	11.2
110	198.7	199.26	0.56	240	4360	4372.5	12.5
120	274.9	275.26	0.36	250	5160	5173.0	13.0
130	372.65	373.92	0.37	260	6079	6080.8	1.8
140	495.8	496.73	0.93	270	7105	7104.8	-0.2
150	649.05	651.0	1.95	280	—	8254.9	—

*Iodobenzene.*

Temp.	Pressure.			Temp.	Observed.	Calculated.	Diff.
	Observed.	Calculated.	Diff.				
30°	1.48	1.48	0.00	160°	367.3	367.43	+0.13
40	2.74	2.73	-0.01	170	479.7	480.4	0.07
50	4.85	4.83	-0.02	180	618.7	619.26	0.56
60	8.30	8.24	-0.06	190	793.0	787.88	-5.12
70	13.65	13.57	-0.08	200	991.0	990.60	-0.40
80	21.78	21.64	-0.14	210	1232.0	1232.0	0.00
90	33.50	33.50	0.00	220	1520.0	1517.1	-2.9
100	50.23	50.44	+0.21	230	1854.0	1851.5	-2.5
110	73.88	74.04	0.16	240	2246.0	2241.2	-4.8
120	105.4	106.16	0.76	250	2700.0	2693.2	-6.8
130	148.3	148.96	0.66	260	3218.0	3214.9	-3.0
140	204.9	204.89	-0.01	270	3815.0	3815.0	0.0
150	276.7	276.70	0.00	280	—	4503.4	—

*Specific Gravities and Molecular Volumes.*

With the larger quantities of liquid, readings of volume were taken at each tenth degree from 30° to 270° or 280°, and also at a little below the atmospheric temperature with the tube cooled by a current of cold water. The volumes at low temperatures were mapped against temperature, the curves continued to 0°, and volumes read off at the temperatures at which specific gravity determinations had been made. In this way, data for two independent calculations of the weight of substance were in each case available.

The data and the calculated weights are given below.

Substance.	Temp.	Volume from curve.	Sp. gr. observed.	Weight in grams.	Mean weight.
Benzene .....	0°	0·3240	0·90006	0·2916	0·2916
	18·0°	0·3309	0·88118	0·2916	—
Fluorbenzene .....	0°	0·5344	1·04653	0·5593	0·5593
	12·86°	0·5422	1·03149	0·5593	—
Chlorobenzene ....	0°	0·5626	1·12786	0·6345	0·6346
	16·0°	0·5714	1·11093	0·6348	—
Bromobenzene .....	0°	0·5216	1·52182	0·7938	0·7938
	14·55°	0·52835	1·50242	0·7938	—
Iodobenzene .....	0°	0·4905	1·86059	0·9126	0·9123
	15·21°	0·4967	1·83798	0·9129	—

The results obtained are given in the following table:—

TABLE IV.—*Benzene.*

Temp.	Volume in c.c.	Vol. of 1 gram.	Molecular volume.	Temp.	Vol. in c.c.	Vol. of 1 gram.	Molecular volume.
0°	—	1·11104	86·483	160°	0·4059	1·3918	108·34
8·6°	0·3275	1·1230	87·42	170	0·4140	1·4198	110·51
14·5	0·3293	1·1294	87·91	180	0·4223	1·4480	112·71
18·0	—	1·13484	88·336	190	0·4315	1·4798	115·19
30·0	0·3358	1·1514	89·63	200	0·4415	1·5139	117·84
40·0	0·3400	1·1661	90·77	210	0·4533	1·5546	121·01
50·0	0·3444	1·1812	91·95	220	0·4661	1·5986	124·43
60·0	0·3489	1·1966	93·15	230	0·4808	1·6487	128·33
70·0	0·3535	1·2124	94·37	240	0·4984	1·7091	133·03
80·0	0·3580	1·2278	95·57	250	0·5198	1·7827	138·76
90·0	0·3626	1·2436	96·80	260	0·5473	1·8770	146·11
100·0	0·3679	1·2615	98·20	270	0·5850	2·0063	156·17
110·0	0·3731	1·2806	99·69	280	0·6460	2·2154	172·45
120·0	0·3791	1·3000	101·19	284·3	0·6921	2·3735	184·75
130·0	0·3854	1·3214	102·86	286·1	0·7150	2·4521	190·87
140·0	0·3919	1·3440	104·61	288·0	0·7563	2·5935	201·87
150·0	0·3989	1·3680	106·49	288·5*	0·8215	2·817	219·3

\* Critical temperature.

*Fluorbenzene.*

Temp.	Volume in c.c.	Vol. of 1 gram.	Molecular volume.	Temp.	Volume in c.c.	Vol. of 1 gram.	Molecular volume.
0°	—	0·95554	91·542	160°	0·6687	1·1957	114·55
10	0·5405	0·9665	92·59	170	0·6818	1·2190	116·78
12·86	—	0·96947	92·875	180	0·6959	1·2442	119·20
30·0	0·5535	0·9897	94·81	190	0·7118	1·2727	121·92
40·0	0·5601	1·0014	95·93	200	0·7291	1·3035	124·88
50·0	0·5667	1·0156	97·30	210	0·7477	1·3369	128·08
60·0	0·5740	1·0263	98·32	220	0·7699	1·3765	131·87
70·0	0·5812	1·0393	99·56	230	0·7949	1·4213	136·16
80·0	0·5890	1·0531	100·89	240	0·8238	1·4729	141·10
90·0	0·5971	1·0676	102·27	250	0·8599	1·5375	147·29
100·0	0·6058	1·0831	103·76	260	0·9074	1·6225	155·44
110·0	0·6148	1·0993	105·31	270	0·9745	1·7424	166·93
120·0	0·6245	1·1166	106·97	275	1·0240	1·8309	175·40
130·0	0·6348	1·1349	108·73	280	1·0896	1·9482	186·64
140·0	0·6454	1·1540	110·55	280·6	—	1·9764†	189·34
150·0	0·6565	1·1738	112·71	*286·55	—	2·435†	233·2

*Chlorobenzene.*

0°	—	0·88664	99·48	130°	0·6451	1·0166	114·06
13·2	0·5696	0·8976	100·71	150	0·6611	1·0418	116·89
15·4	0·5709	0·8996	100·94	160	0·6693	1·0548	118·34
15·6	0·5713	0·9003	101·08	170	0·6784	1·0690	119·94
16·2	0·5717	0·9009	101·01	180	0·6880	1·0841	121·63
16·0	—	0·90015	101·00	190	0·6980	1·0999	123·41
30·0	0·5793	0·9129	102·43	200	0·7087	1·1167	125·29
40·0	0·5851	0·9220	103·44	210·7	0·7210	1·1361	127·47
50·0	0·5908	0·9309	104·45	220	0·7318	1·1531	129·37
60·0	0·5966	0·9402	105·48	230	0·7450	1·1740	131·72
70·0	0·6029	0·9500	106·59	240	0·7595	1·1968	134·28
80·0	0·6091	0·9598	107·69	250	0·7743	1·2201	136·89
90·0	0·6158	0·9704	108·88	260	0·7916	1·2474	139·95
100·0	0·6226	0·9811	110·08	270	0·8100	1·2764	143·21
110·0	0·6297	0·9922	111·33	—	—	—	—
120·0	0·6372	1·0040	112·65	—	—	—	—

\* Critical temperature.

† With smaller quantity, compared at lower temperatures with larger.

*Bromobenzene.*

Temp.	Volume in c.c.	Vol. of 1 gram.	Molecular volume.	Temp.	Volume in c.c.	Vol. of 1 gram.	Molecular volume.
0°	—	0·65711	102·90	140°	0·5971	0·7523	117·80
13·1	0·5273	0·6643	104·03	150	0·6038	0·7607	119·12
14·55	—	0·66559	104·23	160	0·6109	0·7696	120·52
30·0	0·5358	0·6750	105·70	170	0·6179	0·7784	121·90
40·0	0·5406	0·6811	106·65	180	0·6252	0·7876	123·34
50·0	0·5457	0·6875	107·66	190	0·6333	0·7978	124·94
60·0	0·5508	0·6939	108·67	200	0·6412	0·8074	126·44
70·0	0·5562	0·7007	109·73	210	0·6501	0·8190	128·25
80·0	0·5613	0·7071	110·74	220	0·6595	0·8308	130·10
90·0	0·5668	0·7140	111·82	230	0·6684	0·8420	131·85
100·0	0·5726	0·7197	112·96	240	0·6791	0·8555	133·97
110·0	0·5782	0·7284	114·07	250	0·6896	0·8688	136·05
120·0	0·5844	0·7362	115·29	260	0·7019	0·8842	138·46
130·0	0·5906	0·7441	116·52	270	—	0·901*	141·1

*Iodobenzene.*

0°	—	0·53746	109·32	130°	0·5493	0·6018	122·40
10·0	0·4943	0·5415	110·15	140	0·5548	0·6078	123·62
11·0	0·4949	0·5422	110·28	150	0·5603	0·6137	124·83
15·21	—	0·54407	110·66	160	0·5657	0·6198	126·09
15·7	0·4971	0·5446	110·77	170	0·5715	0·6261	127·34
30·0	0·5030	0·5510	112·08	180	0·5777	0·6328	128·72
40·0	0·5074	0·5559	113·06	190	0·5841	0·6399	130·15
50·0	0·5115	0·5603	113·97	200	0·5900	0·6464	131·48
60·0	0·5157	0·5649	114·91	210	0·5960	0·6529	132·81
70·0	0·5205	0·5703	115·99	220	0·6039	0·6616	134·57
80·0	0·5249	0·5750	116·95	230	0·6109	0·6693	136·13
90·0	0·5292	0·5798	117·92	240	0·6182	0·6773	137·75
100·0	0·5345	0·5855	119·10	250	0·6260	0·6858	139·49
110·0	0·5391	0·5906	120·13	260	0·6347	0·6952	141·40
120·0	0·5441	0·5964	121·30	270	0·6441	0·7056	143·51

In calculating the molecular volumes, the following molecular weights were taken:—

Benzene.	Fluorbenzene.	Chlorobenzene.	Bromobenzene.	Iodobenzene.
77·84	95·8	112·2	156·6	203·4

I have not thought it necessary to calculate the constants for any formula such as  $V_t = V_0 + at + bt^2 + ct^3 + \dots$ ; the range of temperature is so great that it is doubtful whether the formula with three constants would reproduce the results with sufficient exactness.

The dilatation of benzene between 0° and 80° has been determined

\* With smaller quantity, compared at lower temperatures with larger.



by several observers, the volumes being given in terms of that at 0° taken as unity. The following table comprises the various results for each 10° :—

*Volume.*

Temp.	Young.	Kopp.	Louguine.	Adricenz.	Pisati and Paternò.
0°	1·0000	1·00000	1·0000	1·00000	1·0000
10	1·0119	1·01190	1·0122	1·01169	1·0118
20	1·0241	1·02410	1·0245	1·02367	1·0244
30	1·0363	1·03665	1·0371	1·03603	1·0368
40	1·0496	1·04961	1·0500	1·04887	1·0500
50	1·0632	1·06302	1·0622	1·06228	1·0636
60	1·0770	1·07692	1·0774	1·07637	1·0776
70	1·0912	1·09136	1·0919	1·09123	1·0921
80	1·1050	1·10641	1·1065	1·10696	1·1070

With the exception of those at 10° and 20°, which were read from a curve, the volumes under my name were calculated from the actual readings. The agreement with Kopp's values is extremely close from 0° to 70°; at 80° it is less satisfactory. A few determinations of specific gravity and vapour-pressure at irregular intervals of temperature are given by Neubeck (*Zeit. physikal. Chem.*, **1**, 654).

*Critical Points of Benzene and Fluorbenzene.*

*Benzene.*—The temperature was raised slightly above the critical point, and observations were taken after lowering the temperature by small stages.

Temperature.

289·25°. No meniscus.

289·1°. Slight fog below; striæ visible on increasing the volume.

288·7°. Permanent mist through the tube, becoming denser on increasing the volume; no meniscus.

288·6°. Very extended cloud, within which the meniscus became visible for a short time on increasing the volume slightly.

288·5°. Meniscus just visible; it disappeared and reappeared on alternately decreasing and increasing the volume.

288·35°. Meniscus quite visible; appearance of rain upwards and downwards, meeting at meniscus.

The critical constants are:—Temperature, 288·5°; pressure, 36·395 mm.; volume of a gram, 2·82 c.c. Sajotschewsky gives 280·6° and 49·5 atm., and Ramsay, 291·7 and 60·4 atm.

*Fluorbenzene.*—The observations were made in the order given :—

## Temperature.

288°. No meniscus or cloudiness.

286·9°. Faint cloudiness near bottom of tube, becoming denser on slightly increasing the volume.

286·7°. Distinct cloudiness near bottom of tube, faint near the top; striae on increasing the volume.

286·45°. Meniscus just visible.

286·65°. Rather dense cloud where the meniscus was.

286·55°. Meniscus appeared or disappeared on increasing or decreasing the volume.

Critical temperature, 286·55°; critical volume, 2·43 c.c.; critical pressure, 33,912 mm.

*Ratios of Absolute Temperatures corresponding to Equal Pressures.*

Curves were constructed from the vapour-pressures recalculated by means of Biot's formula, taking the temperatures as ordinates and logarithms of the pressures as abscissæ. Temperatures corresponding to definite pressures were then read from the curves, the pressures being the same for each substance. The following table gives the temperatures, centigrade and absolute, of the five compounds, corresponding to these pressures, and for comparison, the absolute temperatures calculated in the manner described later, and lastly the differences between the read and recalculated temperatures:—

TABLE V.—*Benzene.*

Pressure.	Temperature.			
	Centigrade.	Absolute.		Difference.
		From curve.	Recalculated.	
20	−5·0	268·0	268·15	+0·15
50	+11·8	284·8	284·75	−0·05
100	26·25	299·25	299·15	−0·1
200	42·4	315·4	315·35	−0·05
400	60·8	333·8	333·75	−0·05
760	80·25	353·25	353·3	+0·05
1000	89·5	362·5	362·55	+0·05
2000	165·55	388·35	388·6	+0·25
3000	132·7	405·7	405·75	+0·05
4000	146·0	419·0	419·05	+0·05
7000	175·05	448·05	448·1	+0·05
10000	196·05	469·05	468·85	−0·2
12000	207·35	480·35	480·15	−0·2
15000	222·1	495·1	495·15	+0·05
20000	242·2	515·2	515·3	+0·1
25000	258·8	531·8	531·7	−0·1
30000	272·9	545·9	545·85	−0·05

*Fluorbenzene.*

Pressure.	Temperature.			
	Centigrade.	Absolute.		Difference.
		From curve.	Recalculated.	
5	—	—	251·0	—
10	-12·35	260·65	261·4	+0·45
20	-0·75	272·25	272·55	+0·3
50	+16·3	289·3	289·3	+0·0
100	30·9	303·9	303·75	-0·15
200	47·25	320·25	320·05	-0·2
400	65·75	338·75	338·55	-0·2
760	85·1	358·1	358·15	+0·05
1000	91·3	367·3	367·4	+0·1
2000	120·25	393·25	393·5	+0·25
3000	137·4	410·4	410·65	+0·25
4000	150·8	423·8	423·95	+0·15
7000	179·8	452·8	452·9	+0·1
10000	200·6	473·6	473·55	-0·05
12000	211·95	481·95	481·8	-0·15
15000	226·7	499·7	499·7	0·0
20000	246·7	519·7	519·7	0·0
25000	263·0	536·0	536·0	0·0
30000	277·0	550·0	550·0	0·0

*Chlorobenzene.*

5	10·35	283·35	283·85	+0·5
10	22·1	295·1	295·25	+0·15
20	35·05	308·05	308·2	+0·15
50	54·1	327·1	327·15	+0·05
100	70·4	343·4	343·5	+0·1
200	88·95	361·95	361·9	-0·05
400	109·8	382·8	382·85	+0·05
760	131·9	404·9	405·0	+0·1
1000	142·4	415·4	415·45	+0·05
2000	172·0	445·0	444·95	-0·05
3000	191·6	464·6	464·35	-0·25
4000	206·9	479·9	479·4	-0·5
7000	239·5	512·5	512·15	-0·35
10000	262·35	535·35	535·5	+0·15
12000	274·75	547·75	548·2	+0·45

*Bromobenzene.*

5	27·9	300·9	300·55	-0·35
10	40·0	313·0	312·65	-0·35
20	53·3	326·3	326·35	+0·05
50	73·3	346·3	346·4	+0·1
100	90·6	363·6	363·7	+0·1
200	110·05	383·05	383·25	+0·2
400	132·3	405·3	405·4	+0·1
760	156·0	429·0	428·85	-0·15
1000	167·05	440·05	439·95	-0·1
2000	198·3	471·3	471·15	-0·15
3000	219·0	492·0	491·7	-0·3
4000	231·95	507·95	507·65	-0·3
7000	269·05	542·05	542·3	+0·25

*Iodobenzene.*

Pressure.	Temperature.			
	Centigrade.	Absolute.		Difference.
		From curve.	Recalculated.	
5	50·6	323·6	323·4	-0·2
10	63·75	336·75	336·4	-0·35
20	78·25	351·25	351·15	-0·1
50	99·75	372·75	372·75	0·0
100	118·3	391·3	391·35	+0·05
200	139·2	412·2	412·35	+0·15
400	163·1	436·1	436·2	+0·1
760	188·55	461·55	461·45	-0·1
1000	200·5	473·5	473·35	-0·15
2000	231·0	507·0	507·0	0·0
3000	256·0	529·0	529·1	+0·1
4000	272·65	545·65	546·2	+0·55

The method of calculation adopted was as follows:—The ratios of the absolute temperatures of each of the substances with that of fluorbenzene were first calculated at each pressure, and these are given in the table below. It will be seen that the ratios of the absolute temperatures of benzene to those of fluorbenzene rise slowly with rise of pressure, but that the other ratios do not exhibit any decided tendency to rise or fall.

TABLE VI.—*Ratios of Absolute Temperatures.*

Pressure.	$\frac{C_6H_6}{C_6H_5F}$		$\frac{C_6H_5Cl}{C_6H_5F}$	$\frac{C_6H_5Br}{C_6H_5F}$	$\frac{C_6H_5I}{C_6H_5F}$
	Calculated.	Recalculated.			
10	—	—	1·1322	1·2008	1·2920
20	0·9844	0·9838	1·1315	1·1985	1·2902
50	0·9844	0·9843	1·1307	1·1970	1·2885
100	0·9847	0·9848	1·1300	1·1964	1·2876
200	0·9848	0·9853	1·1302	1·1961	1·2871
400	0·9854	0·9859	1·1300	1·1965	1·2874
760	0·9865	0·9865	1·1307	1·1981	1·2889
1000	0·9869	0·9869	1·1310	1·1981	1·2891
2000	0·9875	0·9876	1·1316	1·1985	1·2893
3000	0·9885	0·9881	1·1321	1·1988	1·2890
4000	0·9887	0·9885	1·1324	1·1986	1·2875
7000	0·9895	0·9894	1·1318	1·1971	—
10000	0·9904	0·9901	1·1304	—	—
12000	0·9905	0·9904	1·1295	—	—
15000	0·9908	0·9909	—	—	—
20000	0·9914	0·9916	—	—	—
25000	0·9922	0·9921	—	—	—
30000	0·9925	0·9925	—	—	—

The recalculated ratios between benzene and fluorbenzene are given by the equation  $R' = R + c(t' - t)$ , where  $R = 0.9838$ ,  $c = 0.0000313$ ,  $t'$  is the temperature (centigrade) of fluorbenzene, and  $t = 0$ . It will be seen that the recalculated ratios agree remarkably well with those calculated from the temperatures read from the vapour-pressure curves.

In order to judge whether the deviations of the remaining ratios from constancy may be attributed to errors in the experimental work, in the calculation of the constants for Biot's formula, or, lastly, in the graphical construction of the vapour-pressure curves or the reading of temperatures corresponding to definite pressures from those curves, the simplest plan would doubtless be to take the temperatures of one substance, say fluorbenzene, as correct, and to recalculate the absolute temperatures of the other liquids from these, taking the formula  $R' = R + c(t' - t)$  for benzene, and the simple formula  $R' = R$  in the other three cases. But this method of calculation is open to the objection that any small error in the temperature of fluorbenzene would be reproduced in those of the other bodies, and would be exaggerated in the case of the higher boiling substances.

The calculation was therefore made in two stages:—Firstly, the absolute temperatures of fluorbenzene were recalculated from those of each of the other substances, and the mean of all the temperatures at each pressure (including in each case that read from the vapour-pressure curve) were compared with the read temperatures. These mean temperatures are given in Table V under fluorbenzene in the fourth column, and the differences from the read temperatures in the fifth column. It will be seen that the greatest difference  $0.45^\circ$  is, as might be expected, at the lowest pressure, 10 mm. The difference in pressure corresponding to this difference in temperature is  $0.27$  mm. Considering that Regnault's individual observations of the vapour-pressure of water at  $0^\circ$  show an extreme variation of  $0.195$  mm., and that the mean pressures calculated for each of his 12 series of experiments exhibit a maximum difference of  $0.152$  mm., this difference of  $0.27$  mm. in the case of fluorbenzene is perhaps not outside the limit of unavoidable experimental error. It is to be noticed also that the boiling point of fluorbenzene under a pressure of 10 mm. is  $-12^\circ$ , and below  $0^\circ$  the corrections for the thermometer could be obtained only by extrapolation.

Assuming now that these mean temperatures of fluorbenzene are correct, the absolute temperatures of benzene and the other halogen-derivatives were recalculated by means of the same constants as before, and the recalculated temperatures are given and compared with the read temperature in Table V. It will be seen that the greatest error in the whole table is  $0.55^\circ$ , with iodobenzene at the

highest temperature, and it has already been mentioned that this liquid, when in contact with mercury, undergoes slight decomposition at a temperature of  $270^{\circ}$ , even when shielded from the light. From 20 mm. to 3000 mm., the greatest error in the table is  $0.3^{\circ}$ , and below 20 mm. (excluding fluorbenzene) the most serious error is that of chlorobenzene at 5 mm., amounting to  $0.5^{\circ}$ , but in this case the corresponding error in pressure is only 0.15 mm.

Even if the temperatures of fluorbenzene as read from the vapour-pressure curves be taken as the basis of calculation, the errors at pressures at and above 20 mm. are not greatly increased; for benzene, the maximum error is the same,  $+0.25^{\circ}$ , at 400 mm., as against  $+0.25$  at 2000 mm.; for chlorobenzene,  $-0.65^{\circ}$  at 4000 mm., and  $+0.65$  at 12000 mm., as against  $-0.5^{\circ}$  at 4000 mm.; for bromobenzene,  $-0.6^{\circ}$  at 3000 mm. as against  $-0.3$  at 3000 and 4000 mm., and for iodobenzene,  $-0.5$  at 20 mm., as against  $+0.55$  at 4000 mm.

In conclusion it may, I think, be stated that the relations stated below, by means of which the absolute temperatures given in Table V as "recalculated" have been obtained, hold good within the limits of experimental error.

Liquids compared.	Ratios of absolute temperatures at equal pressures.
$C_6H_6/C_6H_5F$	$R' = 0.9838 + 0.0000313t$ ( $t = t^{\circ} \text{C. of fluorbenzene}$ ).
$C_6H_5Cl/C_6H_5F$	$= 1.1308$
$C_6H_5Br/C_6H_5F$	$= 1.1974$
$C_6H_5I/C_6H_5F$	$= 1.2884$
$C_6H_5Br/C_6H_5Cl$	$= 1.0589$
$C_6H_5I/C_6H_5Cl$	$= 1.1394$
$C_6H_4I/C_6H_5Br$	$= 1.0760$

#### *Relations between the Molecular Volumes.*

It seemed likely that any simple relation which may exist between the specific or molecular volumes of different liquids would be most readily found by first comparing closely related substances such as those chosen. The very complete and accurate series of determinations by Thorpe have already led to an important generalisation by Mendeléeff (*Trans. Chem. Soc.*, 1884, 126), and this, combined with the theoretical conclusions of Van der Waals, has in the hands of Thorpe and Rücker afforded a method of calculating the approximate critical temperature of a liquid from its rate of expansion at constant pressure at temperatures below the ordinary boiling point. But it appears to me that one at least of the conclusions of Van der Waals is open to question. In Roth's translation (Leipzig, 1881, 128) of

Van der Waals' Dissertation ("Die Continuität"), the following passages occur:—"Ist für verschiedene Körper die absolute Temperatur derselbe Theil der kritischen Temperatur, so ist auch der Druck des gesättigten Dampfes für dieselben ein gleich grosser Theil des kritischen Drucks . . . so ist auch das Volumen, sowohl das des gesättigten Dampfes, wie das der Flüssigkeit, ein gleich grosser Theil des kritischen Volumens;" and later "Hat man für verschiedene Körper die Grenzcurve construirt—wobei man Druck und Volumen in solchen Maassen nimmt, dass die Culminationspunkte zusammenfallen—so fallen die Curven ganz zusammen."

The first of these laws does not appear to me to be even approximately true. It would be difficult to find two bodies more likely to give results in conformity with the law, if true, than benzene and fluorbenzene. Their boiling points do not differ by so much as 5° at any pressure between 20 mm. and the critical pressure of fluorbenzene so that temperature readings are always on the same part of the thermometric scale, and as the substances were always heated by the vapours of pure liquids boiling under known pressures, there can be no question of the fluctuations of the zero point of a thermometer. Again the critical pressures and temperatures are not very different, the temperatures being especially close together; the compounds are chemically nearly related; moreover the observations have been made by the same observer, by the same method, with the same apparatus, and as nearly as possible at the same time. Even, therefore, if the experimental work is only moderately accurate, any errors in the thermometric scale, in the calibration of the pressure gauges and so on, would have comparatively little influence. Yet the following table shows that when the absolute temperatures of the two bodies are in each case made proportional to the critical temperatures, the corresponding pressures are very far from bearing a constant ratio to each other. On the other hand, the ratios of the molecular volumes at these temperatures are nearly constant, and do not differ seriously from the ratio of the observed critical volumes, but, as will be seen from Table VIII, equally concordant though different results are obtained by taking pressures proportional in each case to the critical pressures.

It will be seen that these ratios are uniformly lower than those in Table VII, but the deviation from constancy is nearly the same in both cases. If the critical volumes could be directly observed with sufficient accuracy, it would of course be possible to decide which of the two methods of comparison gives the better results, but it is unfortunately impossible to reduce the possible error with either substance below from 0·5 to 1 per cent.

Before comparing benzene and fluorbenzene at "corresponding"

pressures and "corresponding" absolute temperatures, I had made a comparison of the molecular volumes of all five liquids at their

TABLE VII.

Absolute critical temperature of benzene..... 561.5 }  
 " " fluorbenzene.. 559.55 } Ratio, 1.0035.

Absolute temperatures.		Vapour-pressures.		Ratios.	Molecular volumes.		
Fluorbenzene.	Benzene.	Fluorbenzene.	Benzene.		Fluorbenzene.	Benzene.	Ratios.
272.25	273.2	20	26.79	1.340	91.47	86.50	0.9457
320.25	321.35	200	252.9	1.265	96.80	91.73	0.9476
367.3	368.6	1000	1190.0	1.190	102.90	97.62	0.9487
423.8	425.3	4000	4550.0	1.137	112.64	106.90	0.9491
473.6	475.25	10000	11080.0	1.103	125.04	118.54	0.9480
519.7	521.5	20000	21750.0	1.088	145.08	137.80	0.9498
550.0	551.9	30000	32320.0	1.077	179.40	169.95	0.9473
559.55	561.5	33912	36395.0	1.073	233*	219*	0.9410

TABLE VIII.

Critical pressure of benzene..... 33395 }  
 " " fluorbenzene.. 33192 } Ratio, 1.0732.

Pressures.		Boiling points (Centigrade).		Molecular volumes.		Ratios.
Fluorbenzene.	Benzene.	Fluorbenzene.	Benzene.	Fluorbenzene.	Benzene.	
20	21.46	- 0.75	- 3.75	91.47	86.10	0.9413
50	53.66	+ 16.30	+ 13.25	93.30	87.87	0.9418
100	107.30	30.90	27.90	94.92	89.41	0.9420
200	214.60	47.25	44.15	96.80	91.23	0.9425
400	429.30	65.75	63.30	99.05	93.51	0.9441
750	815.60	85.10	82.65	101.59	95.91	0.9441
1000	1073.00	94.30	91.95	102.90	97.12	0.9438
2000	2146.00	120.25	118.30	107.00	100.96	0.9438
4000	4293.00	150.80	149.50	112.64	106.35	0.9442
7000	7513.00	179.80	179.15	119.14	112.48	0.9441
10000	10732.00	200.60	200.30	125.04	117.95	0.9433
12000	12879.00	211.95	212.00	128.80	121.55	0.9437
15000	16098.00	226.70	227.05	134.64	127.12	0.9441
20000	21464.00	246.70	247.50	145.08	137.20	0.9457
25000	26831.00	263.00	264.10	158.40	149.80	0.9457
30000	32197.00	277.00	278.60	179.40	169.50	0.9448
33912	36395.00	286.55	288.50	233*	219*	0.9400

\* Direct observations of critical volumes.



boiling points under equal pressures, and it is a remarkable fact that under these conditions the molecular volumes of the halogen-derivatives of benzene bear a constant ratio to each other, but not to those of benzene.

In the following table are given the molecular volumes of the four liquids at their boiling points under definite pressures, and also the molecular volumes recalculated in the same manner as the absolute temperatures in Table V on the assumption that the ratios are really constant. The recalculated volumes of fluorobenzene are the means of those calculated from the other halogen-derivatives and the volumes read from the curve. The volumes of the other halogen-derivatives are recalculated from these mean volumes of fluorobenzene.

TABLE IX.—*Fluorobenzene.*

Pressure.	Molecular volume.			Pressure.	Molecular volume.		
	From curve.	Recalcu- lated.	Diff.		From curve.	Recalcu- lated.	Diff.
5	—	89·33	—	1000	102·90	102·95	+0·05
10	—	90·34	—	2000	107·00	106·99	—0·01
20	91·47	91·48	+0·01	3000	110·03	110·05	+0·02
50	93·30	93·25	—0·05	4000	112·64	112·61	—0·03
100	94·92	94·84	—0·08	7000	119·14	119·22	+0·08
200	96·80	96·74	—0·06	10000	125·04	125·07	+0·03
400	99·05	99·03	—0·02	12000	128·80	128·85	+0·05
760	101·59	101·64	+0·05	—	—	—	—

*Chlorobenzene.*

5	100·45	100·44	—0·01	1000	115·75	115·76	+0·01
10	101·60	101·58	—0·02	2000	120·24	120·30	+0·06
20	102·89	102·86	—0·03	3000	123·69	123·74	+0·05
50	104·88	104·85	—0·03	4000	126·65	126·62	—0·03
100	106·63	106·64	+0·01	7000	134·08	134·05	—0·03
200	108·75	108·78	+0·03	10000	140·68	140·60	—0·08
400	111·32	111·35	+0·03	12000	144·94	144·93	—0·01
760	114·26	114·28	+0·02	—	—	—	—

*Bromobenzene.*

5	105·47	105·41	—0·06	760	119·94	119·93	—0·01
10	106·65	106·60	—0·05	1000	121·47	121·48	+0·01
20	107·99	107·95	—0·04	2000	126·24	126·25	+0·01
50	110·04	110·03	—0·01	3000	129·86	129·86	0·00
100	111·89	111·91	+0·02	4000	132·90	132·88	—0·02
200	114·10	114·15	+0·05	7000	140·75	140·68	—0·07
400	116·81	116·86	+0·05	—	—	—	—

*Iodobenzene.*

Pressure.	Molecular volume.			Pressure.	Molecular volume.		
	From curve.	Recalculated.	Diff.		From curve.	Recalculated.	Diff.
5	114.04	114.09	+0.05	400	126.48	126.48	0.00
10	115.32	115.38	+0.06	760	129.86	129.81	-0.05
20	116.79	116.84	+0.05	1000	131.56	131.49	-0.07
50	119.03	119.10	+0.07	2000	136.72	136.65	-0.07
100	121.09	121.13	+0.04	3000	140.63	140.56	-0.07
200	123.52	123.56	+0.04	4000	143.73	143.83	-0.10

The ratios calculated from the molecular volumes read from the curves are given in Table X, those of benzene to fluorbenzene being included. It will be seen that these, after rising very slowly from 50 to 400 mm. pressure, fall slowly at first, then more and more rapidly with rise of pressure, while the ratios between the molecular volumes of the halogen-derivatives remain almost constant at all pressures.

TABLE X.

Pressure.	Ratios of <i>read</i> molecular volumes at equal pressures.			
	$\frac{C_6H_6}{C_6H_5F}$	$\frac{C_6H_5Cl}{C_6H_5F}$	$\frac{C_6H_5Br}{C_6H_5F}$	$\frac{C_6H_5I}{C_6H_5F}$
20	—	1.1248	1.1806	1.2768
50	0.9401	1.1241	1.1794	1.2758
100	0.9403	1.1233	1.1788	1.2757
200	0.9405	1.1234	1.1787	1.2760
400	0.9410	1.1239	1.1793	1.2771
760	0.9410	1.1248	1.1808	1.2783
1000	0.9407	1.1249	1.1805	1.2785
2000	0.9395	1.1241	1.1802	1.2781
3000	0.9392	1.1241	1.1802	1.2781
4000	0.9387	1.1244	1.1799	1.2760
7000	0.9364	1.1254	1.1814	—
10000	0.9339	1.1250	—	—
12000	0.9321	1.1253	—	—
15000	0.9297	—	—	—
20000	0.9251	—	—	—
25000	0.9163	—	—	—
30000	0.8919	—	—	—

The recalculation of the molecular volumes of the four halogen-derivatives is based on the assumption that the following relations hold good:—

Substances compared.	Ratios of molecular volumes at boiling points under equal pressures.
$C_6H_5Cl/C_6H_5F$	$R = 1.1244$
$C_6H_5Br/C_6H_5F$	1.1800
$C_6H_5I/C_6H_5F$	1.2772
$C_6H_5Br/C_6H_5Cl$	1.0494
$C_6H_5I/C_6H_5Cl$	1.1359
$C_6H_5I/C_6H_5Br$	1.0824

It would, no doubt, be unjustifiable to assert that these relations are absolutely true, but that they represent the facts with very considerable accuracy is, I think, shown by the fact that in Table IX the greatest difference between the read and recalculated molecular volumes amounts to only 0.084 per cent.

If Van der Waals' laws were all true for these closely related compounds, it would follow that the critical pressures of the four halogen-derivatives of benzene must be equal or nearly so, that the ratios of the absolute critical temperatures must be the same as the ratios of the absolute temperatures at any other equal pressures, and that the ratios of the molecular volumes at the critical points must be the same as those at any other equal pressures.

These calculated values would be:—

Substance.	Critical pressure.	Critical temperature.		Critical volume (molecular).
		Absolute.	Centigrade.	
Chlorobenzene..	33912	633°	360°	262
Bromobenzene..	„	670	397	275
Iodobenzene....	„	721	448	298

It is quite impracticable to determine the critical constants of bromobenzene and iodobenzene by the method employed in this research, but I have succeeded in obtaining determinations of the critical constants of chlorobenzene by heating the tube with the vapour of mercury boiling under slightly increased pressure. It will be seen from the data below that as far as chlorobenzene at any rate is concerned the supposition stated above is correct, and it is therefore very probably true for bromobenzene and iodobenzene also. Confirmatory evidence is also afforded by Thorpe and Rücker's relations between the critical temperatures and the dilatations from 0° to the boiling points.

*Experimental Data for Chlorobenzene at very High Temperatures.*

Temperature. Centigrade.	Pressure.	Molecular volume.	Molecular volumes and temperatures calculated from those of fluorben- zene at the same pressures by means of the constants given.	
330·0°	23935	175·0	174·7	329·6°
350·0	36103	202·9	202·3	349·15
(1) { 359·95	—	253·1	—	—
{ 360·2	33824	255·0	—	{ 359·4
(2) { 360·55	33926	262·0	—	{ 359·8
(3) { 360·8	33998	275·0	—	{ 359·95

(1) Meniscus flat. (2) Meniscus unsteady and indistinct. (3) Probable critical point: meniscus just visible, but very unsteady, and it frequently disappeared. (4) Approximately. (5) Roughly.

361·1°. Dense fog and striæ, just possible to detect meniscus occasionally. The frequent disappearance of the meniscus at 360·8° and its occasional appearance at 361·1° are probably due to slight fluctuations of temperature.

361·3°. Faint mist, becoming denser in one part of the tube on increasing the volume considerably.

The reading of volume near the critical point was extremely difficult owing to condensation of globules of mercury on the tube and jacket, and to the fluctuations of temperature which caused the meniscus, when visible, to change its position constantly. No such difficulties were experienced with benzene or fluorbenzene.

The agreement of the critical temperature and pressure with those suggested as probable from the comparison with fluorbenzene is very satisfactory: as regards the volume, which is undoubtedly far less accurately determined, it will be noticed that at 360·55°, at which temperature the pressure is almost identical with the critical pressure of fluorbenzene, the molecular volume 262 is the same as that calculated from the critical volume of fluorbenzene. Considering the uncertainty of the reading at 360·8°, I think it is not too much to say that the observed critical volume shows a rough agreement with that calculated.

The following values may be taken as the critical constants of chlorobenzene:—

Temperature .....	360·55° to 360·8°.
Pressure .....	33926 to 33998 mm.
Molecular volume .....	262 to 275 c.c.

*Thorpe and Rücker's Relations.*

From theoretical considerations, Professors Thorpe and Rücker deduce the equation  $a = \frac{TV_t - 273}{T_1(V_t - 1)}$ , where  $T$  and  $T_1$  are the boiling point and the critical temperature of a substance on the absolute scale, and  $V_t$  is its volume at the boiling point, the volume at  $0^\circ$  being taken as unity. The value of  $a$  is found to vary within comparatively narrow limits for a considerable number of substances, and from seven compounds investigated by Sajotschewsky the mean value 1.995 is obtained. Taking this mean value as correct, Thorpe and Rücker calculate the expansion of benzene between  $0^\circ$  and  $80^\circ$  by means of the equation  $V_t = V_0 \cdot \frac{aT_1 - 273}{aT_1 - T}$ , giving  $T_1$  the value observed by Sajotschewsky, 553.8. If, however, the critical point given in this paper be taken, the agreement with the observed results from  $0^\circ$  to  $60^\circ$  becomes much closer, and if, further, the value of  $a$  be taken as 1.9855 the agreement with my results up to  $80^\circ$  becomes very satisfactory, as will be seen from the following table:—

*Expansion of Benzene.*

Temperature.	$a = 1.995$ , $T_1 = 553.8$ .	$a = 1.995$ , $T_1 = 561.5$ .	$a = 1.9855$ , $T_1 = 561.5$ .	Young.	Kopp.
$0^\circ$	1.0000	1.0000	1.0000	1.0000	1.0000
20	1.0216	1.0212	1.0243	1.0241	1.0241
40	1.0505	1.0496	1.0499	1.0496	1.0496
60	1.0778	1.0762	1.0767	1.0770	1.0769
80	1.1064	1.1043	1.1050	1.1050	1.1064

It is noticeable that Sajotschewsky always finds lower critical temperatures than other observers.

Having determined the expansions and critical temperatures of fluorbenzene and chlorobenzene, I was able to calculate the values of  $a$  for these two bodies. The values obtained are given below.

Fluorbenzene.		Chlorobenzene.	
Temperature.	$a$ .	Temperature.	$a$ .
$80^\circ$	2.030	$120^\circ$	2.050
90	2.021	130	2.036
—	—	150	2.020

At the boiling points under normal pressures, the values of  $a$  for the two substances would not differ greatly from 2.03, and if we may

assume that the values of  $a$  for the two other halogen-derivatives of benzene are approximately the same, it becomes possible to calculate the critical temperatures of bromobenzene and iodobenzene by an entirely different method from that previously adopted.

In the equation  $T_1 = \frac{TV_t - 273}{2.03(V_t - 1)}$  I have taken for bromobenzene the volumes at the two temperatures  $150^\circ$  and  $169^\circ$ , and for iodobenzene those at  $180^\circ$  and  $190^\circ$ . The mean results are—

Bromobenzene, critical temperature....	675.5
Iodobenzene                   ,,                   ,,                   ....	721.0

The absolute temperatures obtained by the previous method are  $670^\circ$  and  $721^\circ$ .

This close agreement of the critical temperatures, as calculated by the two methods, makes it extremely probable that the critical pressures of the four halogen-derivatives of benzene are identical or very nearly so.

The results obtained may be summarised as follows :—

1. When the four halogen-derivatives of benzene are compared together at such temperatures that their vapour-pressures are equal, these temperatures, expressed on the absolute scale, and also the corresponding specific volumes, bear a constant ratio to each other.

2. The critical pressures of fluorbenzene and chlorobenzene, and in all probability those of bromobenzene and iodobenzene, are equal, hence the critical temperatures and volumes may be calculated from the observed temperatures and volumes at any other equal pressures.

3. When benzene is compared with fluorbenzene at such temperatures that their vapour-pressures are equal, neither these (absolute) temperatures nor the corresponding specific or molecular volumes bear a constant ratio to each other.

4. The ratios of the absolute temperatures of benzene and fluorbenzene corresponding to equal pressures are very exactly expressed by the equation  $R' = R + ct$ , where  $R'$  is the ratio at a pressure for which the corresponding centigrade temperature of fluorbenzene is  $t$ ;  $R = 0.9838$ , and  $c = 0.0000313$ .

5. If the specific volumes of benzene and fluorbenzene are compared at temperatures corresponding to pressures which are in all cases proportional to the critical pressures of the two liquids, the ratios of the volumes are very nearly constant. If, again, the specific volumes are compared at absolute temperatures which are always proportional to the absolute critical temperatures, the ratios of the volumes are again nearly constant. But the two methods of comparison are not—as stated by Van der Waals—equivalent, and they cannot both be correct, for it cannot be taken as even approximately true that the

absolute temperatures corresponding to pressures which are always proportional to the critical pressures are themselves proportional to the absolute critical temperatures. Moreover, the values obtained by the two methods of comparison are not quite the same, and for two liquids which are chemically dissimilar the values may differ considerably.

It is impossible at present to say with certainty which method of comparison gives the better results, but I am inclined to think that the comparison at proportional or "corresponding" pressures is more likely to be correct.

6. The relations of Van der Waals, as regards "corresponding" temperatures, pressures, and specific volumes of liquid hold good accurately in the case of the halogen-derivatives of benzene, but since the critical pressures are equal, the comparisons must always be made at *equal* pressures.

7. Fluorine, chlorine, bromine, and iodine belong to the same group in the periodic table; the effect of substituting one of these elements for another in the compounds of the type  $C_6H_5R$ , as regards the relations between vapour-pressure, temperature, and specific volume, is extremely simple, but if hydrogen be substituted for one of the halogens the changes produced are much greater.

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#### XLIX.—*The Molecular Weights of the Metals.*

By Professor W. RAMSAY, Ph.D., F.R.S.

THE means at the disposal of chemists for determining the molecular weights of elements or compounds have, until recently, been limited to the determination of their vapour-densities. Starting with Avogadro's assumption, which by the investigation of the kinetic theory of gases has now been given the precision of a law, the relative weights of gases under similar conditions of temperature and pressure are proportional to the relative weights of their molecules. The standard of reference is hydrogen, which on chemical grounds is supposed to exist in the free state as a diatomic molecule, and this assumption has been rendered almost certain by Kundt and Warburg's determination of the ratio of the specific heat of mercury gas at constant volume to that at constant pressure, whereby it is shown that all the energy imparted in the form of heat to gaseous mercury can be accounted for by supposing it to impart increased translational velocity to the molecule; no energy appears to be absorbed, produc-

ing internal oscillation of *parts* of a molecule. Hence the conclusion that the atom of mercury constitutes the molecule. Naumann, moreover, has pointed out that that energy which disappears in producing internal work when presumably diatomic gases, such as oxygen, hydrogen, nitrogen, carbon monoxide, &c., are heated, and which doubtless causes oscillation or rotation of the atoms within the molecule, in all probability bears a constant proportion to the translational energy of the gaseous molecules. Such gases as NO, CO, HCl, &c., are not easily conceived other than diatomic; hence oxygen, nitrogen, and hydrogen may, from their similarity of behaviour as regards heat with these unmistakably diatomic gases, be also regarded as diatomic.

The method of replacement by stages, although it has rendered excellent service in determining the molecular weights of compounds and, indirectly, the atomic weights of elements, is from its very nature not adapted to the determination of the molecular weights of elements. A knowledge of the molecular weight of potassium chloride, for example, throws no light on the molecular weight of the element potassium, although it may serve as an assistance in deducing the atomic weight of potassium from its equivalent.

On the supposition, then, that the molecular weight of hydrogen is expressible by the formula  $H_2$ , the vapour-density method has fixed the molecular weights of the following elements in the state of gas:—

	Name.	Molecular formula.	Investigators.
<i>Monatomic</i> .....	Mercury ..	Hg .....	Dumas; V. Meyer.
" .....	Cadmium ..	Cd .....	Dewille and Troost.
" .....	Zinc .....	Zn .....	Mensching and V. Meyer.
" .....	Sodium ..	Na .....	Scott.
" .....	Potassium ..	K .....	Scott.
<i>Diatomic, changing to monatomic at high temperatures</i>	Iodine ....	$I_2$ and $I$ .....	Dumas; Dewille and Troost; V. Meyer; Crafts and Meier.
	Bromine ..	$Br_2$ and $Br?$ ..	Jahn; V. Meyer and Zublin.
	Chlorine ..	$Cl_2$ and $Cl?$ ..	Ludwig; V. Meyer; Crafts.
<i>Diatomic, not altered by rise of temperature</i> .....	Hydrogen ..	$H_2$ .....	Regnault; V. Meyer.
	Oxygen ..	$O_2$ .....	Regnault; Jolly; V. Meyer.
	Nitrogen ..	$N_2$ .....	" " "
<i>Triatomic</i> .....	Ozone .....	$O_3$ .....	Andrews and Tait.
	Phosphorus ..	$P_4P_2(?)$ .....	Dumas; Dewille and Troost; V. Meyer.
<i>Tetratomic</i> .....	Arsenic ....	$As_4 \cdot As_2(?)$ ..	Mitscherlich; Dewille and Troost; V. Meyer.
	Antimony ..	$Sb_4(?)Sb_2(?)$ ..	V. Meyer.
	Sulphur ....	$S_6(?)S_2$ .....	Dumas; Bineau; Dewille and Troost; V. Meyer; Biltz.
<i>Hexatomic, changing to diatomic at high temperatures</i> ....	Selenium ..	$Se_6(?)Se_2$ .....	Dewille and Troost.
	Tellurium ..	$Te_6(?)Te_2$ .....	Dewille and Troost.



About the molecular formulæ of mercury, cadmium, zinc, sodium, and potassium there can be no doubt, so far as the gaseous density reveals them; nor are those of hydrogen, oxygen, and nitrogen uncertain. But the remaining elements in this table, which, it may be remarked in passing, are all commonly called non-metallic, exhibit densities varying with temperature, and from what we know regarding similar behaviour of compounds, and especially of those which dissociate into like molecules, it may be concluded that they exist in different molecular aggregates, according to their pressure and their temperature. It is, to say the least of it, remarkable that the majority of elements, about the molecular complexity of which anything is known, should exhibit such a marked contrast to the majority of compounds, where dissociation is the exception and not the rule.

The theory of the analogy between the condition of matter in dilute solutions and in gases under moderate pressure and moderately high temperature, so beautifully developed by Van't Hoff (*Phil. Mag.*, Aug., 1888), and the clear and incontrovertible deduction of the necessary sequence of Raoult's law of the connection between the molecular weight of a dissolved substance and the depression of the vapour-pressure of the solvent, or the lowering of its melting point, have placed in the hands of chemists a new means of investigating the molecular weights of substances inconvenient or impossible to gasify. This method has been applied to the determination of the molecular weights of the following elements:—

*Method of Depressing the Vapour-pressure of the Solvents.\**

Iodine dissolved in solvents with brown colour . . . .	$I_4$ .
Iodine dissolved in solvents with violet colour . . . . .	$I_2$ to $I_4$ .

*Method of Depressing the Melting Point of the Solvent.†*

Bromine in water and in acetic acid . . . . .	$Br_2$ .
Iodine in benzene (very dilute) . . . . .	$I_2$ .
„ (more concentrated) . . . . .	$I_2$ to $I_4$ .
Sulphur in benzene . . . . .	$S_8$ .
Phosphorus in benzene . . . . .	$P_2$ to $P_4$ .

It would thus appear that iodine, like phosphorus and arsenic, but at far lower temperatures, tends to form a molecule of the complexity  $I_4$  whilst the complexity of the sulphur molecule at low temperatures is confirmed (see Biltz, *Zeit. physikal. Chem.*, 2, 920; also Ramsay, *ibid.*, 3, 67).

\* Loeb, *Zeit. physikal. Chem.*, 2, 606.

† Paternò and Nasini, *Ber.*, 21, 2153.

It is unlikely that the method of vapour-densities will render any further service in determining the molecular weights of other elements. Their temperatures of volatilisation are so high that Dumas' method, the only one adapted to settle the point decisively, cannot be employed.

It occurred to me that by using mercury as solvent, many of the metals might be investigated. But as Raoult's method presupposes a knowledge of the molecular weight of the solvent, the question arises, what is the molecular weight of liquid mercury? I think it very unlikely, in view of the investigations of Dr. S. Young and myself, that in condensing from gas to liquid the molecular weight of mercury is altered. Our experiments with stable liquids, such as the alcohols and ether, have shown that their molecular formulæ are not increased, even at low temperatures, when the vapours are in contact with their respective liquids. And further proof, which cannot be gainsaid, of the non-association of mercury-atoms is furnished by the research of Kundt and Warburg, previously alluded to (*Pogg. Ann.*, **127**, 497; also **135**, 337 and 527). It will be remembered that they showed that the total energy communicated to mercury vapour as heat, *even when the vapour was in contact with liquid mercury*, was employed in effecting translational motion of the molecule, whence it may be concluded that even the saturated vapour of mercury consists of single atoms. Hence it appears just to consider the molecular weight of liquid mercury as equal to its atomic weight, 200.

The simple formula connecting the molecular weight of the dissolved substance with the depression of vapour-pressure which the dissolved substance produces in the solvent is—

$$MW = \frac{M'W' \times P \times p}{100 \times d};$$

where MW is the molecular weight to be found; M'W' the molecular weight of the solvent; P/100 the percentage weight of dissolved substance in the solution;  $p$ , the vapour-pressure of the solvent; and  $d$ , the depression in the vapour-pressure of the solvent produced by adding the substance dissolved.

This expression becomes for mercury as solvent—

$$MW = \frac{200 \times P \times p}{100 \times d} = \frac{2P.p}{d}.$$

*Apparatus Employed.*—The first form of apparatus used was a U-tube, one limb of which was about 160 mm. long, and sealed; about 30 mm. from the sealed end a trap was provided. The other limb was about 400 mm. in length, and was connected at its upper end by sealing with a gauge standing in the same trough with a

barometer-tube of similar bore. This U-tube was jacketed with pure bromonaphthalene, which, by means of the arrangement described on another occasion (*Phil. Trans.*, 1887, A, p. 59), could be made to boil under various pressures alterable at will; hence it was possible, from data given in the *Trans.*, 1885, 640, to heat the U-tube to such temperatures as  $260^{\circ}$  or  $270^{\circ}$ , with the certainty that the error in temperature was a small one.

Previous to the experiment, the U-tube was filled with the required amalgam, and all air was expelled by boiling it past the trap. The U-tube was then placed in position, and a little more mercury was added. Both limbs of the U-tube were graduated in millimetres, so that, when the mercury fell in the shorter limb and rose in the longer one, the difference of pressure in the two limbs could be read. But as the open end of the U-tube was connected with a gauge, it was possible to vary the position of the mercury in both limbs, and so to obtain a set of readings at the same temperature.

To control the accuracy of the process, determinations were made of the vapour-pressures of mercury alone at  $260^{\circ}$  and  $270^{\circ}$ . In the following table all the data are given, so as to afford an idea of the method and its trustworthiness:—

*Temperature  $260^{\circ}$ . Pressure under which Bromonaphthalene boiled 488.95 mm. at  $19.5^{\circ}$ , the Atmospheric Temperature.*

Open.	Close.	Gauge.	Barometer.	$\Delta_1$ .	$\Delta_2$ .	$\Delta'_1$ .	$\Delta'_2$ .	$\Delta_3$ .
mm.	mm.	mm.	mm.					mm.
61.0	25.4	276.8	145.5	35.6	131.3	34.0	130.8	96.8
61.0	25.5	276.7	145.5	35.5	131.2	33.9	130.7	96.8
55.4	31.0	266.3	145.65	24.4	120.65	23.3	120.2	96.9
49.2	37.0	254.95	145.9	12.2	109.05	11.65	108.65	97.0
49.1	36.95	254.9	145.95	12.15	108.95	11.60	108.55	96.95
44.4	41.7	245.95	146.0	2.7	99.95	2.6	99.55	96.95
44.4	41.6	245.9	146.0	2.8	99.9	2.7	99.50	96.80
							Mean ..	96.87

In this table, the first two columns refer to the U-tube, the open end being the one connected with the gauge.  $\Delta_1$  and  $\Delta_2$  are respectively the differences between the readings in the U-tube and those of the gauge and barometer.  $\Delta'_1$  is  $\Delta_1$  corrected from  $260^{\circ}$  to  $0^{\circ}$ ;  $\Delta'_2$ ,  $\Delta_2$  corrected from  $19.5^{\circ}$  to  $0^{\circ}$ ;  $\Delta_3$  is the difference between the two, and gives the observed vapour-pressure of mercury.

At  $270^{\circ}$ , the following results were obtained:—

*Pressure under which Bromonaphthalene boiled, corrected to Atmospheric Temperature, 21°, 771 mm.*

Open.	Close.	Gauge.	Barometer.	$\Delta_1$ .	$\Delta_2$ .	$\Delta'_1$ .	$\Delta'_2$ .	$\Delta_3$ .
mm.	mm.	mm.	mm.					mm.
78·8	7·95	337·3	145·0	70·85	192·3	67·4	191·6	124·2
78·8	7·95	337·2	145·0	70·85	192·2	67·4	191·5	124·1
68·6	17·8	318·9	145·15	50·8	173·75	48·3	173·15	124·85
68·4	18·0	318·7	145·1	50·4	173·6	47·9	172·95	125·05
59·4	26·95	301·3	145·3	32·45	156·0	30·85	155·45	124·6
59·35	27·0	301·25	145·25	32·35	156·0	30·75	155·45	124·7
51·4	34·8	286·5	145·4	16·6	141·1	15·8	140·6	124·8
47·65	38·0	279·9	145·5	9·65	134·4	9·15	133·9	124·75
47·75	37·9	279·85	145·45	9·85	134·4	9·35	133·9	124·55
43·7	41·9	272·0	145·55	1·8	126·45	1·70	126·0	124·3
43·8	42·0	272·05	145·6	1·8	126·45	1·70	126·0	124·3
							Mean ..	124·56

We have here two determinations of the vapour-pressure of mercury, viz., at 260°, 96·87 mm., and at 270°, 124·56 mm. These figures assume that the vapour-pressures of bromonaphthalene have been correctly determined at these temperatures. The vapour-pressures of bromonaphthalene were determined by Dr. Sydney Young and myself by the method described by us in *Trans.*, 1885, 42. But we have also shown (*Trans.*, 1886, 47), that the vapour-pressures of mercury follow the law pointed out by us in the *Philosophical Magazine* for December, 1885, and January, 1886; and that it is possible from two trustworthy observations of the vapour-pressures of a substance at any two temperatures not too close to each other, to calculate the temperature corresponding to any vapour-pressure below 6000 mm. By means of these relations we calculated the vapour-pressures of mercury at intervals of 5° from 135° to 520°. The calculated vapour-pressure of mercury at 260° is 96·66 mm. I have now found 96·87 mm. The difference, 0·21 mm., corresponds to an error in temperature of the bromonaphthalene of 0·27°; and at 270°, the calculated vapour-pressure of mercury is 123·90 mm.; whereas the vapour-pressure found is 124·56 mm., the difference is 0·66 mm., corresponding to a difference in temperature of 0·21°. The error as thus calculated may be wholly ascribable to the determination of the vapour-pressures of bromonaphthalene, in which case those given by Dr. Young and myself are at such temperatures low by a pressure equivalent to about 0·2°; or it may be ascribed to error in the determination of the vapour-pressures of mercury. I am disposed to believe the former supposition; but whichever be taken, the difference

is a minute one for such high temperatures, and the observations furnish further proof of the accuracy of the work already referred to.

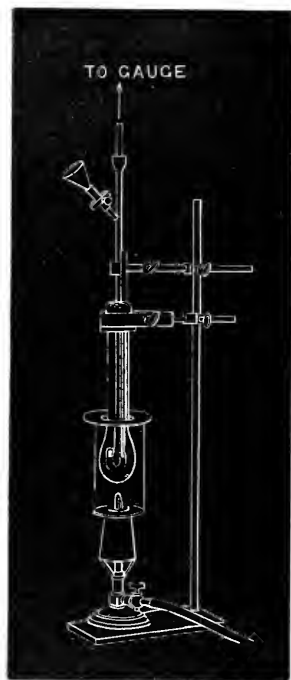
In carrying out similar experiments on amalgams by means of this apparatus, two difficulties were met with which led to its abandonment. These were, first, the difficulty of introducing the amalgams of easily oxidisable metals without considerable oxidation; this caused a difference in the surface tension of the mercury in the closed limb and the open limb of the U-tube; and although it is easy to introduce such a correction as would approximately restore the surfaces of the mercury to the position which they would occupy on the scale provided both menisci were plane surfaces, yet this correction does not show the true position of the mercury, inasmuch as a greatly curved meniscus means that the mercury is considerably depressed in that limb of the tube on which the meniscus is so curved. It is impossible to estimate the value in millimetres of this depression; and hence no allowance is possible. This unknown error may bear a considerable proportion to the whole depression observed, which is not a very great one. The second difficulty is, that the solubility of many metals in mercury at  $260^{\circ}$  or  $270^{\circ}$  is very slight. Now as the depression of the vapour-pressure of mercury by a dissolved metal depends on the total amount of metal dissolved, and is inversely proportional to the molecular weight, a very weak solution cannot be employed, else the probable error bears too large a proportion to the total quantity measured. But the results of measurements with cadmium and with sodium bear out the conclusions of subsequent experiments, hence they are worth quoting here. I should mention that attempts were also made to determine the behaviour of zinc, magnesium, barium, and silver, but owing to the oxidation of the first three of these metals during their introduction, the glass was wetted by the metal, and it was almost impossible to obtain readings; with silver, the solubility was too small at  $270^{\circ}$  to permit of trustworthy measurements.

1. *Cadmium*.—Temperature =  $260^{\circ}$ ; percentage in amalgam, 2.074; vapour-pressure (mean of 11 measurements), 93.02 mm.; highest measurement, 93.6 mm.; lowest, 92.2 mm.; calculated molecular weight, 104.1; temperature =  $270^{\circ}$ ; percentage, the same; vapour-pressure (mean of 9 measurements) 120.17 mm.; highest measurement, 120.75 mm.; lowest, 119.45 mm.; calculated molecular weight, 117.7; mean of both determinations, 110.9; atomic weight of cadmium, 112.1.

2. *Sodium*.—Temperature =  $270^{\circ}$ ; percentage in amalgam, 0.6255; vapour-pressure (mean of 13 measurements), 112.9 mm.; highest

measurement, 114.2 mm.; lowest measurement, 111.3 mm.; calculated molecular weight, 13.36; atomic weight of sodium, 23.04.

Owing to the difficulty of experiment, this process was abandoned in favour of a simpler one. A U-tube with a shorter limb was employed, of the shape shown in the figure. Close beside, almost in



contact with it, was a perfectly similar U-tube. Both of these tubes were surrounded by a bath of mercury vapour. The one containing the amalgam was connected with a gauge standing in the same trough with a barometer so that the pressure could be slightly altered, and various separate readings of pressure could be taken. As the temperature of the boiling mercury was not invariably that corresponding to the atmospheric pressure of the day, some slight difference being always caused by radiation, or by convection currents, the second U-tube, which contained pure mercury, served to correct the reading; for, had the temperature been exactly that of mercury vapour, the levels of the mercury in the two limbs of the second U-tube would have been the same; this was sometimes the case; but as a rule, the temperature of the bath was slightly below that of the temperature of the vapour of boiling mercury at the pressure of the day, and by sub-

tracting the difference in level of the mercury in the two limbs of the second U-tube from the height of the barometer, the pressure truly corresponding to the temperature of the mercury vapour was obtained.

In this way, a series of determinations at the boiling point of mercury were obtained; it was unnecessary to know the temperature, for that corresponded to the pressure of the atmosphere of the day, subject to the correction mentioned.

Various methods of filling the experimental U-tube with amalgam were resorted to, according to the nature of the metal experimented with. The usual method of procedure was as follows:—The tube was pumped empty by means of a Sprengel's pump, and hydrogen was admitted to restore the pressure. The tube was again evacuated, and the amalgam, previously prepared, was introduced through the side-tube. The determinations having been made, the percentage composition of the amalgam was ascertained by analysis. This plan was pursued with oxidisable metals, such as lithium, sodium, potassium, barium, and manganese. With metals easily obtained and not readily oxidisable, the requisite amount of mercury, weighed out, was introduced into the tube. The tube was then exhausted and filled with hydrogen; the metal, weighed out, was dropped on to the mercury, and the stopper replaced; and the tube was again exhausted and again filled with hydrogen. Before each experiment, the contents of the U-tube were well boiled for about an hour under diminished pressure, so that all gas might be carried round the bend. On increasing the pressure, it is necessary that the mercury column should quickly touch the glass, leaving no trace of a gas-bubble. During each experiment, often between each two readings, the pressure was again reduced so as to ensure the expulsion of any residual gas. It was seldom found that this operation was necessary, for, as a rule, the readings obtained were identical within the limits of experimental error.

The proportion which the experimental error bears to the result obtained differs in each individual case. It was not common to obtain two readings from any set with so great a difference as 1 mm. in pressure. But when the total lowering of vapour-pressure amounts to 10 mm. this represents an extreme error of 10 per cent. In cases where larger amounts were used the error was proportionately smaller, and often did not amount to more than 1 or 2 per cent. The mean result is of course still more trustworthy.

The source of an error which cannot be very great, and yet which cannot well be estimated, has been previously mentioned, viz., that the form of the meniscus in the closed limb differs from that in the open limb. Here it is not the mere differences in level which

require correction, that can easily be approximated to, and has been uniformly allowed for; it is the unknown diminution or increase in pressure produced by the tendency of the curved surface to occupy a lower position in the tube than a plane surface would. The general concordance of the results would, however, show that this error is not a serious one. The depression in one limb is partially balanced by that in the other, and the algebraic sum is probably negligible.

The results will now be considered in the order in which the metals occur in the periodic table:—

1. *Lithium*.—Prepared by electrolysing a solution of the chloride, mercury forming the negative electrode. Long, lustrous, needle-shaped crystals separated on standing, which rapidly become dull, and melted on exposure to air. The constants were determined, and the lithium in the portion of amalgam employed was subsequently estimated as chloride. The amalgam was admitted through the side tube.

2. *Sodium*.—Sodium amalgam, prepared in the usual way, was employed. It was admitted through the side-tube into a rarefied atmosphere of hydrogen. Five sets of experiments were made, the percentage of sodium in the amalgam being different in each case. The sodium was afterwards estimated as chloride.

3. *Potassium*.—The results with potassium amalgam were similarly obtained, two sets of experiments being made.

4. *Barium*.—Barium amalgam was prepared in the same manner as lithium amalgam. Before introducing it into the U-tube, it was warmed so as to bring all the barium amalgam into solution. When cold it was filled with needle-shaped crystals. After the experiments had been made, the barium was estimated as sulphate.

5, 6, and 7. Repeated attempts were made to prepare beryllium, calcium, and strontium amalgams in a similar manner, but without success. The amalgams can be made, but are so easily attacked by water, even when the tube in which the electrolysis took place was surrounded by a freezing mixture, that they were not of sufficient concentration to give trustworthy results. All of them oxidise very rapidly on exposure to air, beryllium amalgam becoming covered with a black film, whilst strontium and calcium are covered by a grey film of oxide. During the electrolysis of calcium chloride, the solution is filled with black particles; this is not the case with strontium or barium. Attempts were also made, but without success, to prepare the metals by the electrolysis of the fused chlorides; for no coherent lumps were obtained which would have been suitable for such determinations. The depression produced by these amalgams was always too small to give trustworthy results. The result for calcium, however, will be given in its place, but it must not be considered as of any great value.



8. *Magnesium*.—A sample of commercial magnesium was sublimed in a vacuum by heating it to redness in a piece of hard combustion tubing. It sublimed with difficulty; but the resulting metal had a silver-white colour, and was obviously pure. A weighed piece was dropped on the surface of the mercury in the U-tube; the tube was then exhausted and filled with hydrogen. Two sets of experiments were made with different quantities.

9. *Zinc*.—This metal was also carefully purified by distillation in a vacuum. The pure zinc was barely attacked by hydrochloric acid, even at boiling temperature. The method was the same as with magnesium. Three sets of experiments were made.

10. *Cadmium*.—The sample was also purified by distillation. Three sets of experiments were made.

These amalgams are also unstable in moist air. The amalgam of magnesium turns black, and it was conjectured that the black substance might prove to be a suboxide of magnesium; but on analysis it proved to be a mixture of magnesia with finely divided mercury. Zinc amalgam is more stable in air than magnesium amalgam; and the cadmium compound may be exposed for some time without much oxidation.

11. *Aluminium*.—A sample of aluminium wire, which contained on analysis 99.1 per cent. of aluminium, was employed. It was cut into short lengths and dropped into a weighed amount of mercury contained in the U-tube. After exhaustion and filling with dry hydrogen, the aluminium dissolved readily on boiling the mercury. The resulting amalgam possesses a most curious property. A drop, allowed to stand in ordinary air, sends out a loose, porous, white mass of aluminium oxide, which grows from hour to hour and presents the appearance of a long, white worm, often attaining the length of a foot. All the aluminium is thus expelled from the mercury, and the alumina may be ignited and weighed. Two sets of experiments were made.

12. *Gallium*.—By the kindness of M. Lecoq de Boisbaudran, I was furnished with 0.5 gram of gallium. It dissolved easily in the mercury. One estimation was made. The gallium amalgam does not tarnish in air.

13. *Thallium*.—A sample of commercial thallium was purified by precipitation as chloride, and reduction by fusion with potassium carbonate and cyanide. The amalgam is easily made, and does not tarnish. Five experiments were made.

14. *Tin*.—The metal was reduced from the dioxide as with thallium. The amalgam is stable in air. Two experiments were made.

15. *Lead*.—The metal was prepared from the chloride, as above. Two sets of readings were taken.

16. *Arsenic*.—Attempts to prepare an amalgam of arsenic failed;

the element is insoluble in mercury, even at the boiling point of mercury; and on electrolysis of the dilute chloride, the element is deposited on the surface of the mercury; none enters into solution. Hence experiments could not be carried out.

17. *Antimony*.—Antimony dissolves in mercury freely at the boiling point, but crystallises out in spangles on cooling. The amalgam is permanent in air; four estimations were made.

18. *Bismuth*.—Two experiments were made with this amalgam. It is permanent in air.

19. *Copper*.—Although copper amalgamates readily, yet its amalgam is almost insoluble in mercury, even at the boiling point, giving too small a depression of vapour-pressure, hence experiments made with it failed.

20. *Silver*.—The same remark applies to silver. But the amalgam is much more soluble in boiling mercury than the corresponding one of copper. One set of readings was taken. The composition of the amalgam, after it has been heated to dull redness, appears to be  $\text{HgAg}$ .

21. *Gold*.—This amalgam is also not freely soluble; yet sufficient dissolved for the purpose.

22, 23. *Platinum and Palladium*.—These metals do not dissolve in mercury to a sufficient extent to make it possible to carry out experiments.

24, 25. *Iron and Nickel*.—Attempts to produce these alloys by electrolysis succeeded in so far as dilute solutions were obtained; but the amount present was too small to allow of an estimation of their molecular weights.

26. *Manganese*.—This element was amalgamated by electrolysis of its chloride. The amalgam rapidly turns black in air, but may be preserved for some time under water in a closed vessel, on which it has little or no action. Under alcohol, in an open vessel, it rapidly becomes oxidised, owing to absorption of the oxygen of the air. A successful series of readings was obtained.

The results of these experiments are given in the table (p. 533).

On inspecting the table it will be seen that the molecular weights of the elements lithium, magnesium, zinc, cadmium, gallium, tin, lead, bismuth, silver, and gold are expressed by numbers almost identical with their atomic weights. But here the question of probable error of experiment should be considered. It may be taken that no two readings of any set differed by more than a millimetre. The total depression with different elements, however, is represented by numbers of very different magnitude. Thus with the smallest quantity of sodium taken, 0.86 atom per 100 atoms of mercury, the mean total depression observed was 6.7 mm. The probable error is, however,

*Tabulation of Results.*

	No. of readings.	Percentage.	No. of atoms per 100 atoms of mercury.	Pressure of mercury vapour.	Depression.	Molecular weight found.	Atomic weight.
				mm.	mm.		
(1.) Lithium .....	7	0·0597	1·70	763·6	12·9	7·1	7·02
(2.) Sodium .....	7	0·0985	0·86	736·4	6·7	21·6	23·04
(3.) „ .....	8	0·1768	1·54	767·2	15·0	18·1	„
(4.) „ .....	9	0·2147	1·87	766·8	17·9	18·3	„
(5.) „ .....	9	0·3205	2·79	755·0	29·3	16·5	„
(6.) „ .....	7	0·6616	5·35	772·1	62·7	15·1	„
(7.) Potassium .....	9	0·3023	1·53	752·8	15·6	29·1	39·14
(8.) „ .....	7	0·0180	5·26	742·5	49·6	30·2	„
(9.) Calcium .....	8	0·0373	0·19	750·4	2·9	19·1	40·08
(10.) Barium .....	9	0·6107	0·90	762·0	12·3	75·7	137·00
(11.) Magnesium .....	5	0·0855	0·70	758·0	5·4	24·0	24·30
(12.) „ .....	5	0·5820	4·82	749·8	40·6	21·5	„
(13.) Zinc .....	6	0·3459	1·07	751·7	7·4	70·1	65·43
(14.) „ .....	7	0·6282	1·93	766·1	15·5	62·1	„
(15.) „ .....	5	1·0214	3·16	755·4	23·6	65·4	„
(16.) Cadmium .....	5	0·04187	0·75	752·6	6·3	100·2	112·1
(17.) „ .....	5	1·0785	1·95	753·4	16·3	99·7	„
(18.) „ .....	5	1·9220	3·51	740·0	27·4	103·8	„
(19.) Aluminium .....	7	0·2043	1·52	755·0	8·4	36·7	27·01
(20.) „ .....	9	0·3950	2·94	758·5	18·1	33·1	„
(21.) Gallium .....	5	0·7855	2·27	767·1	17·3	69·7	69·9
(22.) Thallium .....	4	0·8191	0·81	758·9	7·6	163·6	204·2
(23.) „ .....	9	1·666	1·66	745·6	13·3	186·8	„
(24.) „ .....	4	2·894	2·92	765·5	24·6	180·1	„
(25.) „ .....	5	3·290	3·33	759·8	25·3	197·6	„
(26.) Tin .....	6	1·142	1·94	754·1	14·7	117·4	119·1
(27.) „ .....	5	2·292	3·94	753·4	23·1	149·5	„
(28.) Lead .....	4	2·020	2·00	762·1	15·4	199·9	206·93
(29.) „ .....	5	4·348	4·39	762·6	26·5	250·2	„
(30.) Antimony .....	5	1·117	1·86	769·6	12·6	136·5	120·30
(31.) „ .....	5	1·526	2·58	742·6	14·3	158·5	„
(32.) „ .....	5	2·257	3·84	754·2	17·2	197·9	„
(33.) „ .....	5	3·289	6·22	755·4	16·5	301·2	„
(34.) Bismuth .....	5	3·772	3·77	762·1	26·8	214·5	208·1
(35.) „ .....	5	4·636	4·68	763·9	30·5	232·2	„
(36.) Manganese .....	6	0·3122	1·14	755·0	8·5	55·5	55·0
(37.) Silver .....	5	1·709	3·22	750·0	22·8	112·4	107·93
(38.) Gold .....	6	1·541	1·59	760·4	11·3	207·4	197·22
(39.) „ .....	6	2·690	2·80	742·5	19·2	208·1	„

reduced by the number of observations, and cannot be considered so great as 1 mm. It would have been easily possible to calculate the true mean probable error; but the result would have given a fallacious impression of the amount of error. For, as has been previously remarked, there is a source of error impossible to estimate, due to

unequal capillary depression in the open and closed limbs of the U-tube. It must however be held that those measurements in which a large depression was observed are more accurate than measurements of a small depression, inasmuch as the total quantity measured bears a much greater proportion to the sources of error.

The element sodium, present in small proportion to the solvent mercury, has apparently a molecular weight lower than the atomic weight, the number 21.6 being found, whereas the atomic weight is 23. On increasing the proportion of sodium, the apparent molecular weight falls, till with 5.35 atoms per 100 atoms of mercury, the number 15.1 is reached. This behaviour is not observable with potassium, the numbers obtained with 1.55 and 5.26 atoms of metal per 100 atoms of mercury being sensibly identical. The low number cannot be due to the existence of stable alloys of these metals with mercury, for if these were present a higher and not a lower weight would be observable. One possible cause, and that appears an improbable one, is that the presence of sodium tends to produce an association of atoms of mercury so that it would no longer be justifiable to assume the atomic weight of mercury as identical with its molecular weight. It may, on the other hand, be the case that a definite stable alloy of sodium and mercury is formed, with a definite vapour-pressure, and that such a substance acts as a solvent. It is, however, remarkable that lithium, an element closely related to sodium, gave no sign of such irregularity, while alteration of dilution with potassium is apparently without influence on the molecular weight, which nevertheless was found lower than the atomic weight, viz., 29 and 30, instead of 39.

But little weight can be attached to the result with calcium; the difficulty of producing a sufficiently concentrated amalgam hindered any further experimental investigation. Various attempts were made without success. But with both calcium and barium the same peculiarity is seen, viz., molecular weights lower than the atomic weights of these elements. No doubt the cause of this behaviour, whatever it may be, is the same as determines it with sodium; but as a study of the influence of varying amounts did not throw light on the anomaly with sodium, series of experiments with metals much more difficult to manipulate were not executed.

Perhaps the same tendency may account for the results with magnesium; but as the total depression with 0.7 atom present per 100 of mercury amounted to only 7.4 mm., too much weight must not be attached to the number 24.0. With cadmium, again, the numbers obtained are somewhat low; and about these results there can be no doubt; the cadmium was free from zinc, and was redistilled in a vacuum before use.

The metal thallium, of which the atomic weight is approximately 204, again gives low results, varying from 164 to 198; but the tendency is here to rise with increase of metal proportionately to solvent. Still there can be no doubt here as to the molecular weight indicated.

The metals tin, lead, antimony, and bismuth show distinct tendency towards association of atoms. The more concentrated the amalgam the higher the apparent molecular weight. As regards the number 301.2, obtained for antimony, with 6.22 atoms per 100 of mercury, such a high result may well be due to the limit of solubility of antimony in mercury having been reached. The amalgam, on cooling, was filled with crystals of antimony, and there may well have been free antimony in the hot amalgam. This would have the effect of apparently raising the molecular weight; for that portion which did not dissolve in the mercury would still appear on the numerator of the fraction in the equation given on p. 524, and would cause the quotient to be too high. I do not think that this was the case with 3.84 atoms of antimony present per 100 of mercury, for the amalgam on cooling deposited few crystals. And the remark is also inapplicable to the three metals tin, lead, and bismuth, all of which are readily soluble in mercury.

The metals gallium, silver, and gold give numbers sufficiently near their atomic weight to render it probable that the molecule and atom are with them identical.

The only other elements to be considered are manganese, with which the normal number was obtained, and aluminium, which gave invariably high results. Good commercial aluminium was used, which on analysis was found to contain over 99 per cent. of that metal. The result can hardly be attributed to impurity, but must be connected in some way with the metal itself. The numbers 36.7 and 33.1 were found instead of 27. It is possible but not probable that such a high result is due to association of atoms; for very different amounts were used in each case, viz., 1.52 atoms and 2.94 atoms per 100 atoms of mercury.

It is interesting to compare these results with those of two experimenters who have published their results since the preliminary note of this research was read. Messrs. Heycock and Neville made use of the method of freezing in a similar series of observations; their preliminary note is published in the *Proceedings of the Chemical Society*, 1889, No. 65. Employing tin as solvent, they find concordant results for the metals zinc, copper, silver, cadmium, lead, and mercury. The elements antimony and aluminium gave abnormal results. With antimony they obtained a rise, connected possibly with the formation of a compound of antimony and tin, and its serving as

solvent; and with aluminium the fall was only  $1.34^{\circ}$  per atom of metal per 100 atoms of solvent instead of about  $2.4^{\circ}$ . This would imply a high molecular weight for aluminium; in fact, assuming the other metals to have molecular weights identical with their atomic weights, the molecular weight of aluminium should be represented by the formula  $Al_2$  when dissolved in tin.

G. Tamman has also published a memoir in Ostwald's *Zeitschrift für physikalische Chemie*, 1889, 441, in which he gives results similar to those of Messrs. Heycock and Neville. He used mercury as solvent, and with the metals potassium and sodium obtained what he considers normal results; taking as the molecular depression of freezing point of mercury  $425$ , the mean numbers for these metals are  $424$  and  $420$ . Very dilute solutions were used, varying from  $0.048$  atom to  $0.353$  atom per 100 atoms of mercury. With thallium and with zinc, lower numbers were obtained, viz.,  $365$  and  $390$ , while with bismuth the number  $570$  expresses incipient association. With lead, cadmium, gold, and tin his results, when only small amounts were employed, were also normal; but with larger amounts, either association of atoms or formation of stable alloys occurred, rendering the results inconclusive.

Similar experiments, in which sodium was employed as solvent, gave erratic results—in every case appearance of association of atoms being observed. But Tamman points out that it is improbable that such association can take place, as it would contradict experience. We have, however, no knowledge of molecular weights of metals at low temperatures; which, moreover, are eminently favourable to chemical association of atoms to form molecules. No opinion can be pronounced on Tamman's suggestion in the present state of our knowledge. It is, however, noteworthy that the solvent in this case is a substance which gives curious results as regards its own molecular weight as determined by the boiling point method; and it may be that its molecular aggregation is disturbed by the presence of foreign metals dissolved in it.

So far, then, as conclusions can be drawn from these experiments, it would appear legitimate to infer that in solution, as a rule, the atom of a metal is identical with its molecule, as the physical properties of those metals which have been vaporised would lead us to suppose.

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L.—*The Amount of Nitric Acid in the Rain-water at Rothamsted, with Notes on the Analysis of Rain-water.*

By R. WARINGTON, F.R.S.

THE earliest analyses of the rain-water at Rothamsted published by Lawes and Gilbert (*Brit. Ass. Report*, 1854), do not include the determination of nitric acid; attempts were indeed made to determine the amount present, but the method used proved inadequate for this purpose. Way subsequently determined the nitric acid in samples of Rothamsted rain-water, representing the rainfall of each month in 1855 and 1856 (*J. Roy. Agri. Soc.*, 1856, 142, 618; 1886, 12). To accomplish these determinations he made use of the reaction proposed by Bunsen: the residue obtained by evaporating the rain with lime-water was heated with potassium iodide and hydrochloric acid in a flask free from oxygen, and the liberated iodine determined. By this process he obtained a mean of 0.12 of nitrogen as nitric acid per million of water, the extreme amounts in the rainfall of any month being 0.06 and 0.30 per million. The total quantity of nitric nitrogen in the rainfall of each year was respectively 0.72 lb. and 0.76 lb. per acre.

In 1869 and 1870, Dr. E. Frankland examined 71 samples of rain-water from Rothamsted for nitric acid. He found that his usual method (the production of nitric oxide gas by the action of the water residue mixed with sulphuric acid upon mercury) failed to show the presence of nitric acid. Thirty-four of the samples of rain-water were, however, examined by the aluminium method, and in each case nitric acid was found. The arithmetical mean of these 34 analyses gives 0.14 of nitrogen as nitric acid per million of water, the extremes being 0.01 and 0.44 per million. In samples of dew, a maximum of 0.50 was obtained. As the samples of rain examined did not represent the whole rainfall of any period, they do not afford material for calculating the average composition of rain-water; the mean result of the 34 analyses agrees, however, substantially with the earlier results obtained by Way.

In recent years, new determinations of the ammonia, chlorine, and sulphuric acid in rain-water have been made at the Rothamsted Laboratory (*Trans.*, 1887, 501); we have now to record similar results relating to nitric acid.

The rain-water employed, as in all the determinations already noticed, was collected in a large leaden gauge, having an area of 1-1000th of an acre. Of the daily collection of rain, dew, or snow-

water, a fixed fraction (a gallon for each inch) was placed in a carboy; at the end of each month the contents of the carboy was mixed, and a sample taken for analysis. In the carboy receiving the rain for nitric acid estimation, a little mercuric chloride was placed each month, with the view of preventing any change of ammonia into nitric acid; it may be doubted, however, if this precaution was necessary, as the rain-water always contained a very appreciable amount of lead, and earlier experiments (*J. Roy. Agri. Soc.*, 1883, 319) showed that on the whole the rain-water more frequently gained than lost ammonia by keeping.

The method first employed was to concentrate 10 lbs. of the rain-water in a retort, a little magnesia being added to decompose any ammonium nitrite or nitrate present. The concentration was conducted in a retort, as earlier experiments had shown (*Trans.*, 1881, 229) that evaporation in the open air, and especially over gas, resulted in a distinct addition to the nitrites present. When concentrated to a small bulk, the water was filtered, and then evaporated nearly to dryness in a very small beaker. The nitrogen as nitrates and nitrites was then determined by the improved form of Schloesing's method already described (*Trans.*, 1882, 345), the amount of nitric nitrogen being ascertained by measurement of the nitric oxide gas obtained.

My own experiments had shown Schloesing's method to be susceptible of great accuracy, and to be quite unaffected by the presence of organic matter. Suspicion was, however, aroused that nitrates were lost during the final stage of concentration of the water. In some cases, depending apparently on the amount of organic matter present, a heavy black deposit, probably of reduced lead, was formed when the water reached a small bulk, and from this deposit bubbles of gas were continuously evolved. Fearing the reduction of nitrates, I sought to control the results by some method in which the concentration of the water should be unnecessary. The aluminium method seemed open to objection, as it involved the addition of much sodium or potassium hydrate, which would probably react on the nitrogenous organic matter in the rain-water and produce ammonia. I resolved, therefore, to try the copper-zinc couple, following the plan proposed by M. W. Williams (*Trans.*, 1881, 100).

In the experiments first made, ammonia was determined in one portion of the rain-water; the nitrates and nitrites were then reduced by means of the couple in another portion of the water, and ammonia again determined; from the difference in the quantity of ammonia found in the first and second determination, the quantity of nitrogen originally present as nitrates and nitrites was calculated. This mode of proceeding was soon rejected as admitting of little exactness. As



the determinations of ammonia were made by Nesslerising, the quantity of ammonia present in the second determination was necessarily small, and the greater part of this consisted of the ammonia originally present in the rain; the errors of two determinations thus fell on the very small amount of ammonia representing the nitrates and nitrites in the water.

The method finally adopted was to boil rapidly 1 litre of the rain-water in a retort, with a little magnesia (previously raised to a low red heat and then washed), till 250 c.c. had distilled over. The residue was then made up to 800 c.c., transferred to a wide-mouthed stoppered bottle, supplied with strips of zinc foil converted into couple, and placed in an incubator at 21—24° for three days.\* A measured portion of the solution was then distilled, and the ammonia in the distillate determined.

This plan had two advantages: 1. The ammonia, as well as the nitrogen as nitrates and nitrites, could be determined in the course of the same operation, and in the same sample of water. For this purpose it was only necessary to fit the retort to an efficient condenser, and to remove all ammonia from the apparatus by boiling distilled water in the retort before introducing the rain-water. The distillate of 250 c.c. afterwards obtained was well mixed, and the ammonia present determined in 25, 50, or 100 c.c., diluted to 150 c.c. with water free from ammonia. 2. The nitrogen as nitrates and nitrites was determined directly and alone; the error of the determination was also as small as Nesslerising admits of, since it was possible, if necessary, to distil 600 c.c. of the boiled rain-water (corresponding to 750 c.c. of original rain), and thus obtain a full amount of ammonia for determination, even when the rain had been poor in nitrates.

Some of the monthly samples of rain-water were analysed both by the Schloesing and by the copper-zinc method, with the results given in the next table.

On comparing the results given by the two methods, it appears that in a number of cases the differences shown are very small; whilst in fewer instances, generally where the rain-water is of a more concentrated character, the copper-zinc method shows a considerably larger amount of nitric acid. In 11 samples of rain, the mean amount of nitric nitrogen found by Schloesing's method was 0.125, and by the copper-zinc method 0.162 per million of water. The original suspicion was thus confirmed. The lower result obtained by the use of

\* This time is a good deal longer than that mentioned by Williams. It is perhaps unnecessarily long; but the condition of the solution naturally determines a very slow action. The disappearance of nitrites, as shown by metaphenylenediamine, is in this case no safe indication of the completion of the reaction, as the amount of nitrous nitrogen will frequently be too small to give a reaction with this test.

*Nitrogen as Nitrates and Nitrites per million of Rain-water.*

Rains analysed.	Schloesing's method.	Copper-zinc method.	Difference.
1886, September .....	0·196	0·270	0·074
„ December .....	0·038	0·048	0·010
1887, January .....	0·111	0·172	0·061
„ March .....	0·163	0·247	0·084
„ August .....	0·366	0·385	0·019
„ September .....	0·081	0·093	0·012
„ October .....	0·094	0·090	0·004
„ November .....	0·069	0·093	0·024
„ December .....	0·064	0·066*	0·002
1888, February .....	0·127	0·229*	0·102
„ March .....	0·068	0·095*	0·027
Mean 11 analyses .....	0·125	0·162	0·037

*Nitrogen as Nitrates and Nitrites in 19 Monthly Rainfalls at Rothamsted (Schloesing's Method).*

	Rainfall.	Nitrogen as nitrates and nitrites.	
		Per million.	Per acre.
	inches.		lb.
1886, September .....	1·51	0·196	0·067
„ October .....	3·94	0·089	0·079
„ November .....	2·77	0·064	0·040
„ December .....	4·21	0·038	0·036
1887, January .....	2·39	0·111	0·060
„ March .....	1·76	0·163	0·065
„ April .....	1·19	0·106	0·029
„ May .....	2·35	0·162	0·086
„ June .....	0·71	0·284	0·046
„ July .....	0·79	0·204	0·036
„ August .....	1·04	0·366	0·086
„ September .....	3·11	0·081	0·057
„ October .....	1·69	0·094	0·036
„ November .....	3·41	0·069	0·054
„ December .....	1·66	0·064	0·024
1888, January .....	0·95	0·198	0·043
„ February .....	0·98	0·127	0·028
„ March .....	3·13	0·068	0·048
„ April ..	2·14	0·145	0·070
Mean of 19 months .....	2·09	0·111	0·052
Total 12 months, May, 1887, to April, 1888 .....	21·96	0·124	0·614

\* These results were obtained with the less exact method first employed.

Schloesing's method in the case of certain rain-waters was probably due, as already suggested, to a reduction of nitrates during the preliminary concentration of the water, and was thus no fault of the method itself.

When this error of deficiency was discovered, the nitrogen as nitrates and nitrites had already been determined during 19 months by Schloesing's method. Since May, 1888, the copper-zinc method, with its accompanying determination of the ready-formed ammonia in the rain, has been exclusively made use of. The results of these analyses are given on page 540 and below.

*Nitrogen as Nitrates and Nitrites in 20 Monthly Rainfalls at Rothamsted (Copper-zinc Method).*

	Rainfall.	Nitrogen as nitrates and nitrites.	
		Per million.	Per acre.
	inches.		lb.
1886, September .....	1·51	0·270	0·092
„ December .....	4·21	0·048	0·046
1887, January .....	2·39	0·172	0·093
„ March .....	1·76	0·247	0·098
„ August .....	1·04	0·385	0·091
„ September .....	3·11	0·093	0·065
„ October .....	1·69	0·090	0·034
„ November .....	3·41	0·093	0·072
1888, May .....	1·28	0·109	0·031
„ June .....	4·87	0·167	0·184
„ July .....	3·86	0·104	0·091
„ August .....	3·38	0·090	0·069
„ September .....	1·03	0·253	0·059
„ October .....	1·09	0·173	0·043
„ November .....	4·46	0·096	0·097
„ December .....	1·69	0·155	0·059
1889, January .....	1·29	0·190	0·055
„ February .....	1·95	0·095	0·042
„ March .....	1·89	0·136	0·058
„ April .....	2·48	0·230	0·129
Mean of 20 months .....	2·42	0·138	0·075
Total 12 months, May, 1888, to April, 1889 .....	29·27	0·139	0·917

A comparison of the average amount of nitric nitrogen found by the two methods again shows that higher results were obtained by the copper-zinc method. Thus the average contents of 19 monthly samples (mean rainfall 2·09 inches) is 0·111 of nitric nitrogen per million by the Schloesing method; whilst the average of 20 monthly

samples (mean rainfall 2·42) is 0·138 per million by the copper-zinc method. The excess by the latter method shown by these figures is also probably below the truth, as the waters analysed in the copper-zinc series represent heavier rainfalls, and consequently weaker waters, than those analysed in the preceding series by Schloesing's method.

The average amount of nitrogen as nitrates and nitrites found by the more exact (copper-zinc) method is 0·138 per million. This is almost exactly the figure representing the arithmetical mean of Frankland's 34 analyses of individual rainfalls, namely, 0·14 per million. It is slightly higher than that found by Way, namely, 0·12 per million; the comparison with Way's results is apparently a fair one, as the average monthly rainfall in the case of his samples was 2·35 inches, and in the case of the present series, 2·42 inches.

In the next table the amount of nitrogen as ammonia, as well as that found as nitrates and nitrites, is given for the 12 months during which the copper-zinc method has been employed.

*Nitrogen as Ammonia, and as Nitrates and Nitrites, in the Rainfall at Rothamsted during 12 months, 1888-89.*

	Rainfall (inches).	Per million of rain.		Per acre (lbs.).	
		Nitrogen as ammonia.	Nitrogen as nitrates and nitrites.	Nitrogen as ammonia.	Nitrogen as nitrates and nitrites.
1888, May .....	1·28	0·256	0·109	0·074	0·031
„ June .....	4·87	0·500	0·167	0·551	0·184
„ July .....	3·86	0·388	0·104	0·338	0·091
„ August ....	3·38	0·288	0·090	0·220	0·069
„ September..	1·03	1·025	0·253	0·238	0·059
„ October....	1·09	0·525	0·173	0·129	0·043
„ November .	4·46	0·313	0·096	0·315	0·097
„ December..	1·69	0·500	0·155	0·191	0·059
1889, January ...	1·29	0·575	0·190	0·168	0·055
„ February ..	1·95	0·238	0·095	0·105	0·042
„ March ....	1·89	0·400	0·136	0·171	0·058
„ April.....	2·48	0·575	0·230	0·323	0·129
Whole year ...	29·27	0·426	0·139	2·823	0·917

With a rainfall slightly above the average, the proportion of nitrogen as ammonia gives a mean of 0·426 per million or 2·823 lbs. per acre.\* The nitrogen as nitrates and nitrites is at the same time 0·139

\* This amount of nitrogen as ammonia is somewhat above the average of five years, already published (Trans., 1887, 502), namely 2·41 lbs. per acre.

per million, or 0·917 lb. per acre. The total nitrogen present as ammonia, and as nitric and nitrous acid, is thus 3·74 lbs. per acre.

The amount of nitrous acid in the Rothamsted rain-water is extremely small, and only to be appreciated by the delicate naphthylamine test.

The quantities of nitric acid found by other investigators have been very various. The average result of the analyses made at seven agricultural stations in Germany and Italy in 1864—72 (*J. Roy. Agric. Soc.*, 1881, 268), representing the rainfall of 13 years, is 0·47 per million of nitrogen as nitric acid, and 1·26 per million of nitrogen as ammonia, the total being 10·18 lbs. of nitrogen per acre per annum. At the Observatory at Moutsouris (Paris) the average of 10 years is 0·70 of nitrogen as nitric acid, and 1·82 of nitrogen as ammonia per million of rain, the total being equal to 12·36 lbs. of nitrogen per acre per annum.

Results recently obtained at Lincoln, New Zealand, and at Tokio, in Japan, agree more closely with the Rothamsted figures. At Lincoln, Professor G. Gray finds, on an average of three years, 0·15 of nitric nitrogen, and 0·096 of ammoniacal nitrogen per million of rain; the total equal to 1·6 lb. of nitrogen per acre per annum. At Tokio, Kellner finds in one year's rain 0·085 per million of nitric nitrogen, or 1·02 lb. per acre. The nitrogen as ammonia in another year's rain was 0·126 per million, or 1·78 lb. per acre.

Müntz and Aubin found only a minute trace of nitrates in rain and snow-water collected at the summit of the Pic du Midi (nearly 3000 m. high); they suggest that nitrates are not produced in the atmosphere at elevations above those at which electrical discharges from clouds occur.

Müntz and Marcano (*Compt. rend.*, 108, 1062) have analysed 121 rainfalls from Caracas (Venezuela); the mean proportion of nitric nitrogen was 0·578 per million, the maximum reached was 4·21 per million. Nineteen rainfalls from St. Denis (Réunion) gave a mean of 0·69 of nitric nitrogen per million. They conclude that the production of nitric acid in the atmosphere proceeds with much more energy in tropical countries.

#### *Notes on the Analysis of Rain-water.*

Rain-water is so seldom systematically analysed that our knowledge of its contents in various localities is very imperfect; it may perhaps, therefore, be of some use to describe very briefly the methods of analysis employed at Rothamsted.

If the average composition of rain-water is to be determined, it is most important that either the *whole* of the rain falling on a given

area should form the sample examined, or that a sample representing the whole rainfall should be prepared by mixing together a fixed fraction of each rainfall. The plan adopted in preparing the monthly samples at Rothamsted has already been described. Averages obtained by taking the mean of many analyses, without regarding the relative quantity of the rainfalls which they represent, are necessarily inexact.

*Ammonia*.—When ammonia is determined by Nesslerising, the direction usually given is to place 400 c.c. or 500 c.c. of the water in the retort, and to distil two or more quantities of 50 c.c.; the total ammonia present is then ascertained by adding together the amounts found in the several distillates. This method may be convenient when nothing is known as to the quantity of ammonia present, but it must generally be attended with a loss of accuracy. The liability to error in comparing the tints given by the ammoniacal distillate, and by the standard solution of ammonia, is not inconsiderable, and is usually estimated as 5 per cent., though this may be reduced by practice. The possible proportion of this error is least at a certain depth of tint, about that given by 2 c.c. of the standard solution of ammonium chloride; with much weaker solutions, the possible error will assume considerably larger proportions. In following the method described above, we have the errors of at least two experiments included in the determination of the ammonia, and one or more of these errors may be proportionally great, from the extreme dilution of the later distillates.

The plan adopted at Rothamsted is to make one determination of ammonia in the whole of the distillate obtained, the strength of which is regulated by varying the amount introduced into the retort, so that it shall be equal to somewhere about 2 c.c. of the standard ammonia solution. A 150 c.c. cylinder is first filled with the rain-water, and 3 c.c. of Nessler's reagent added; the depth of tint indicates what quantity of rain will be required for distillation. The retort and condenser having been freed from ammonia by boiling distilled water and a little magnesia in the retort, the measured amount of rain-water is added to the (cooled) contents of the retort, taking care that the final volume does not exceed 600 c.c.; distillation is then continued till a 150 c.c. cylinder is filled. The determination of ammonia is made in this distillate in the usual way. The five years' determinations of ammonia already referred to were made in this manner. When nitric acid is also to be determined, the ready formed ammonia is obtained in the manner described above.

*Nitric Acid*.—The general mode of determining nitric acid by means of the copper-zinc couple has been already given; the preparation of the couple is the only point requiring further detail. For the 800 c.c. of boiled rain-water I employ six strips of zinc foil, 4 inches long by

1 $\frac{1}{4}$  inches wide; the strips are bent at right angles along their centre to obtain stiffness. The couple is prepared in a series of five beakers, containing respectively a dilute solution of sodium hydrate, very dilute sulphuric acid, 3 per cent. solution of copper sulphate, ordinary distilled water, distilled water free from ammonia. Through these five beakers the zinc-foil is successively passed. It is rinsed both after the alkali and acid, but after the copper has been deposited the strips are simply drained, and carefully placed in the distilled water, it being difficult to rinse without removing the copper. The couple should be entirely submerged when placed in the rain-water.

*Chlorine.*—The method of estimation employed is the one generally made use of in water analysis, namely, titration with solution of silver nitrate, using potassium dichromate as an indicator. The proportion of chlorine in rain is generally too small to be determined with accuracy in the unconcentrated water. Moreover, some rain-waters give at once an orange tint with the reagents employed, giving rise to the idea that chlorine is absent: this orange tint is not discharged by the addition of a chloride. The method adopted at Rothamsted is to add 5 c.c. of lime-water, free from chlorine, to 1 litre of rain-water, and to concentrate the water in an open basin in a quiet room to less than a quarter litre. When cold, the water is filtered through a washed filter into a quarter-litre flask, diluted to a quarter litre, and then used for the determination of chlorine. In water thus prepared a normal reaction is always obtained.

*Sulphuric Acid.*—The rain used for the determination of sulphates is specially collected in a glass funnel, having a small piece of asbestos cloth in the pipe; no vulcanised caoutchouc is employed for connections. 10—15 lbs. of the water are concentrated to a small bulk in a retort, and then filtered through Swedish paper previously washed with hydrochloric acid. Sulphuric acid is then gravimetrically determined in the filtrate with barium chloride. The concentration in a retort is essential, as gas flames are a constant source of sulphuric acid.

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LI.—*The Action of the Chlorides of Propionyl and Butyryl on Phenol.*

By W. H. PERKIN, Ph.D., F.R.S.

As I have been making an examination of the magnetic relations of some of the phenylic ethers of the fatty acids, it has been necessary to prepare several of them in a pure state. The process employed has been the ordinary one of acting on phenol with an acid chloride. It was found, however, that usually the phenylic ether is not the sole product of the reaction, and as I have in two instances to some extent examined into this subject, it was thought that it might be useful if I gave a short account of my observations. They refer to the action of the chlorides of propionyl and butyryl on phenol.

*Action of Chlorides of Propionyl on Phenol.*

A quantity of crystallised phenol was treated with rather more chloride of propionyl than that required by theory for the formation of phenyl propionate. At first the temperature fell very considerably as the phenol dissolved, hydrochloric acid was then gradually evolved, but the mixture did not get warm. After standing for about 20 hours, the product was distilled, the portion coming over between  $202^{\circ}$  and  $230^{\circ}$  being kept separate. The rest did not come over entirely below  $360^{\circ}$ , the last parts crystallising on cooling. A little carbonaceous matter was left in the retort.

The first portion boiling at  $202\text{--}203^{\circ}$  was repeatedly fractioned, and eventually a considerable quantity was obtained, boiling at  $211.5\text{--}212.5^{\circ}$  (corr.); this was considered to be nearly pure phenyl propionate; its density  $d_{15^{\circ}}^{15^{\circ}}$  was 1.04954. On standing, however, during the cold weather the substance became a crystalline mass, and was further purified by draining off the oily products, and then keeping the crystals on a porous plate for some time. Thus purified, phenyl propionate boils at  $211^{\circ}$  (corr.), and has a density of—

$$\begin{array}{ll} d_{4^{\circ}}^{4^{\circ}} 1.06427, & d_{15^{\circ}}^{15^{\circ}} 1.05413, \\ & d_{25^{\circ}}^{25^{\circ}} 1.04672. \end{array}$$

Phenyl propionate crystallises in beautiful, large, transparent prisms, which fuse at  $20^{\circ}$ ; when in the liquid state it may be cooled to  $0^{\circ}$ ,



and kept at that temperature for some time without crystallising. It has been previously prepared but not obtained in the solid state.

The product boiling above  $230^{\circ}$  was again distilled; all that came over below  $250^{\circ}$  was rejected, but the higher parts were saponified by boiling with alcoholic potash, a little water added, and the alcohol boiled off. On the addition of hydrochloric acid, an oil separated which solidified to a crystalline mass. This was purified by being spread out upon a porous plate, and left until all oily products had been absorbed; it was then dissolved in boiling alcohol, in which it was easily soluble, and on cooling was deposited in brilliant, highly refractive crystals consisting of short prisms which often appear as thick, six-sided tables. On analysis, this substance gave the following numbers:—

0.2045 gram of substance gave 0.5390 gram of  $\text{CO}_2$  and 0.1260 gram of  $\text{OH}_2$ .

	Theory for $\text{C}_9\text{H}_{10}\text{O}_2$ .	Found.
Carbon .....	72.00	71.99
Hydrogen .....	6.60	6.84

This substance is therefore isomeric with phenyl propionate. It is easily soluble in alkalis, and there can be no doubt it is a *propionyl-phenol*,  $\text{C}_3\text{H}_5\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ .

It fuses at  $148.5^{\circ}$ , or  $128.5^{\circ}$  higher than phenyl propionate. In boiling water it dissolves to a small extent, and crystallises out as the solution cools. Unlike phenol, it dissolves easily in ammonia, this is probably owing to the chlorous influence of the  $\text{C}_3\text{H}_5\text{O}$  group.

#### *Action of Chloride of Butyryl on Phenol.*

Chloride of butyryl behaves with phenol in a manner similar to chloride of propionyl, very little rise of temperature taking place. The product of the reaction was heated to its boiling point to drive off hydrochloric acid, and when cooled dissolved in twice its volume of ether, the resulting solution was then agitated with dilute potash to remove any phenol, separated, dried with calcium chloride, and distilled. After the ether had come over, the temperature quickly rose to  $227^{\circ}$ , and a considerable quantity of oil came over between this and  $230^{\circ}$ , the temperature then soon rose to  $250^{\circ}$ , leaving a residue in the retort.

On fractioning the first part a few times, a considerable quantity of oil boiling at  $227\text{--}228^{\circ}$  (corr.) was obtained; this was phenyl butyrate; its density determination gave:—

$$d_{4^{\circ}}^{4^{\circ}} 1.03644, \quad d_{15^{\circ}}^{15^{\circ}} 1.02685, \\ d_{25^{\circ}}^{25^{\circ}} 1.01985.$$

All attempts to make the substance crystallise by cooling failed. It has not previously been described.

The residual product left in the retort, and boiling above  $250^{\circ}$ , was distilled under reduced pressure ( $250^{\circ}$  mm.). It commenced to boil at about  $197^{\circ}$ , and the oil which came over between this and  $225^{\circ}$  proved to consist chiefly of phenyl butyrate, and was rejected, the rest came over between  $225^{\circ}$  and  $285^{\circ}$ , the thermometer standing for some time at about  $280^{\circ}$ , which is supposed to represent the boiling point of the oil. This is a thick oil, and could not be solidified by means of a freezing mixture. It was saponified with alcoholic potash, and after the removal of the alcohol, dilute hydrochloric acid added, when an oil separated; the product was then boiled to volatilise butyric acid; on cooling the oily matter solidified to a brown crystalline mass, which was extremely soluble in alcohol, but not easily so in light petroleum; it was therefore first crystallised from this solvent, when it was obtained in brownish crystals, and then from carbon bisulphide in which it is moderately soluble when hot, but nearly insoluble when cold. A black product, however, came down at the same time, but this was separated by recrystallising from petroleum of low boiling point ( $75$ — $100^{\circ}$ ), of which a considerable quantity was required; it was then obtained in white, pearly plates, melting at  $91^{\circ}$ .

This substance gave the following numbers on analysis:—

0.1939 gram of substance gave 0.5216 gram of  $\text{CO}_2$  and 0.1316 gram of  $\text{OH}_2$ .

	Theory for $\text{C}_{10}\text{H}_{12}\text{O}$ .	Found.
Carbon .....	73.17	73.36
Hydrogen .....	7.31	7.54

This substance is therefore isomeric with phenyl butyrate, but as it behaves as a phenol no doubt it is butyrylphenol,  $\text{C}_4\text{H}_7\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ . It dissolves freely in alkalis and in ammonia, it is also soluble to a small extent in boiling water, from which it is deposited in slender needles on cooling.

There can be but little doubt that the propionyl- and butyryl-phenols described above are *para*-derivatives. An experiment was made in reference to this point with propionylphenol; this was converted into its methyl-derivative by treating its potassium compound with methyl iodide, and the product was then oxidised with chromic mixture;

during the oxidation the odour of anisic aldehyde was very perceptible, but no anisic acid was obtained; it is quite likely, however, that the oxidation was carried too far as the amount of product at my disposal was very small.

The formation of these phenols is rather remarkable, as the temperature at which the acid chlorides acted on the phenol was low, unless it occurred afterwards, when heating the product to its boiling point. I have, however, made several experiments in this direction, such as boiling the phenylic ethers either alone or in presence of hydrochloric acid for a long time, or by heating the acid chloride in a sealed tube, but the results have been negative.

There are two ways in which they may be formed. First, the acid radicle in the phenylic ether may pass over into the phenyl, or they may result from the action of the acid chlorides on the phenylic ether. This, however, is not settled, and owing to other work I have not given so much attention to the subject as I could wish.

It is rather remarkable that in the formation of phenyl acetate no high boiling products are obtained. A mixture of phenyl acetate, acetic chloride, and a little chloride of zinc heated in a sealed tube yields a dark-brown tar, containing a colouring matter dissolving in alkalis with a red colour, probably phenacetin. Acetylphenol, however, has been prepared by Klingel (*Ber.*, **18**, 2691), from *amidoacetophenone* by the diazo-reaction. In the preparation of phenyl cœnanthate, high boiling, secondary products were obtained, but not examined.

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### LII.—*Observations on the Melting Points of some Salicylic and Anisic Compounds.*

By W. H. PERKIN, Ph.D., F.R.S.

IN 1867 (*Chem. Soc. J.*, **20**, 418), I brought before the Society an account of some new derivatives of salicyl aldehyde, and amongst other compounds described the methyl- and ethyl-derivatives of this substance. These were described as nearly colourless oils, which did not solidify when cooled by ice and salt. Since then methyl salicyl aldehyde has been re-examined by Voswinckel (*Ber.*, **15**, 2024), who says that if every trace of salicyl aldehyde be removed from it, it is obtained in prisms melting at 35°.

Wishing to measure the magnetic rotation of methyl salicyl aldehyde, some quantity of it was prepared, the process used being

practically that described in my paper already referred to, which consists in heating the sodium compound of salicyl aldehyde with methyl iodide and alcohol; the temperature used was that of the water-bath, instead of  $135\text{--}140^\circ$  as originally given, the lower temperature being sufficient as shown by Voswinckel. The product was diluted with water, the oil taken up with ether, washed with potash to remove any salicyl aldehyde, and the ethereal solution then dried with potassium carbonate and distilled. After the ether had been driven over, the oil boiled at  $243.4\text{--}245.4$  (corr.). This corresponds pretty closely to the uncorrected boiling point given in the previous paper if the correction for stem in the air be added, as it then becomes about  $242.8^\circ$ .

On cooling this methyl salicyl aldehyde by ice and hydrochloric acid, it did not solidify until the sides of the vessel containing it were well rubbed with a glass rod, it then crystallised to a hard mass; on removing it from the freezing mixture, however, it soon became fluid again, and on examining the melting point by a thermometer immersed in the product it was found to be from  $2.7^\circ$  to  $3^\circ$ . A specimen of the product made in 1867 was next experimented with in the same manner, and it behaved in the same way. From these results I was inclined to think that the melting point given in Voswinckel's paper was a misprint, and should be  $3.5$  instead of  $35^\circ$ . Not being satisfied, the methyl salicyl aldehyde was steam-distilled, dissolved in ether, treated with potash, and the ethereal solution dried with potassium carbonate. A small quantity of this solution when evaporated deposited prismatic crystals of the aldehyde, and these had a much higher melting point; the ethereal solution was then distilled, and the methyl salicyl aldehyde came over as a colourless oil boiling at  $243\text{--}244^\circ$  (corr.) at the normal pressure, and at  $199^\circ$  (corr.; constant), at  $250^\circ$  mm. On touching this oil with a crystal obtained by evaporating the ethereal solution, it quickly solidified, and the crystals melted at  $35\text{--}36^\circ$ , and thus the observation of Voswinckel was confirmed. On touching the product prepared in 1867 with a crystal of this substance, it also solidified and then melted at about  $35^\circ$ , and it was found that it was not the difference of purity which caused this great variation in melting point, but that it was due to the substance being dimorphous and the two modifications having distinct fusing points, as the following observations made with the purified specimen showed.

The crystallised product was melted so that not a trace of crystals was left, the resulting oil was then allowed to cool and afterwards further cooled with ice and salt. At first it remained fluid, but on rubbing the sides of the vessel containing it, it soon solidified to a beautiful, white, radiating crystalline mass; this, when removed from the freezing mixture and placed in water of a temperature of  $15^\circ$  very

soon entirely melted and appeared as a clear oil, but on introducing a minute crystal of a specimen melting at  $35^{\circ}$ , it rapidly solidified with evolution of heat to a mass of prismatic crystals having the melting point of  $35^{\circ}$ .

There are but few dimorphous substances in which the differences of the melting points of their stable and unstable modifications vary so greatly as in the case of methyl salicyl aldehyde. This will be seen from the following table:—

	Unstable.	Stable.	Diff.	
Nitrotetrabromobenzene..	$60^{\circ}$	$96^{\circ}$	$36^{\circ}$	V.v. Richter, <i>Ber.</i> , 8, 1127. Perkin, <i>Chem. Soc. J.</i> , 53, 705.
Chloromaleic anhydride..	about 0	$34\cdot5^{\circ}$	$34\cdot5^{\circ}$	
Methyl salicyl aldehyde..	3	$35\cdot5$	$32\cdot5$	
Benzophenone .....	26	49	$23^{\circ}$	Zincke, <i>Annalen</i> , 159, 377.
Meta-chloronitrobenzene..	23	44	21	Laubenheimer, <i>Ber.</i> , 9, 766.
Dibromopropionic acid...	51	65	14	Linnemann and Penl, <i>Ber.</i> , 8, 1099.
Isohydrobenzoïn diacetate	106	118	12	Forst and Zincke, <i>Jahresb.</i> , 1874, 518.
Nitrometa-chloronitrobenzene.	$36\cdot5$	39	$3\cdot5^{\circ}$	Laubenheimer, <i>Ber.</i> , 9, 760.
Tolyl phenyl ketone .....	55	59	3	Zincke, <i>Jahresb.</i> , 1876, 2.

*Ethyl salicyl aldehyde* can be made to crystallise in the same way as the methyl-derivative, but as yet only one kind of crystals has been obtained, and these fuse at about  $6-7^{\circ}$ .

*Anisic Aldehyde*.—This was prepared from the bisulphite compound. it boiled at  $248^{\circ}$  (corr.), and at  $199-199\cdot5^{\circ}$  at 210 mm.; when cooled with ice and salt, it solidified to a crystalline mass. A thermometer placed in the product when melting showed a constant temperature of  $-0\cdot02^{\circ}$ . It is thus seen that anisic aldehyde, although a para-compound, melts at even a lower temperature than that of the unstable crystals of its orthoisomeride, methyl salicyl aldehyde.

*Anisate of Ethyl*.—This boiled at  $269-270^{\circ}$  (corr.), and when cooled in a freezing mixture solidified, the crystalline mass melting at  $7^{\circ}$ . Its isomeride, methyl salicylate of ethyl, boils at  $261\cdot5^{\circ}$  (corr.), and could not be made to crystallise by cooling, these two ethers therefore behave like most para- and ortho-compounds, the para easily crystallising, the ortho being liquid or of lower melting point.

LIII.—On Schützenberger's Process for the Estimation of Dissolved Oxygen in Water.

By Sir HENRY E. ROSCOE, F.R.S., D.C.L., LL.D., and JOSEPH LUNT, B.Sc., Associate of the Owens College.

THE increased use of Schützenberger's method as a means of determining the amount of dissolved oxygen in water, has led us to make a careful critical examination as to its reliability.

The method has been examined recently by Dupré,\* and by Ramsay and Williams (*Chem. Soc. J.*, Trans., 1886, **49**, 751), whose papers may be referred to for a description of the process.

*Results not concordant with the same Water.*—In the first place, 15 careful experiments made with London tap water, with improved apparatus, showed that with every care the oxygen values found for the same sample varied between 4.55 and 6.50, the mean being 5.57, or a difference of 35 per cent. on the mean value.

The object of the present communication is to indicate the cause and the means adopted to eliminate the source of error attaching to these observations.

*High Results when the Titration is performed quickly.*—An indication of the nature of the disturbing influence is obtained by varying the conditions under which the experiment is made.

Thus, if instead of adding the hyposulphite solution drop by drop as in the above-mentioned experiments, it be added quickly and nearly the maximum quantity at once, mixing the liquids thoroughly, and finishing the titration drop by drop, a much higher result is obtained than when the addition is made slowly.

The results of four series of estimations by the slow and quick methods alternately, gave the following hyposulphite values:—

	Slow.	Quick.	Slow.	Quick.
	5.30 c.c.	7.05 c.c.	5.50 c.c.	7.45 c.c.
	4.60	7.55	5.65	7.15
	5.25	6.90	5.35	6.60
	5.75	7.15	5.65	7.05
	5.80	7.25	5.80	7.00
	<hr/>	<hr/>	<hr/>	<hr/>
Means..	5.34 c.c.	7.18 c.c.	5.59 c.c.	7.05 c.c.
	<hr/>	<hr/>	<hr/>	<hr/>

\* *The Analyst*, 1885, **10**, 156, or Sutton's *Volumetric Analysis*. 5th Edition.

This indicates a difference of 47 per cent. on the mean of the 20 estimations.

*Low Result when the Water has been exposed to Hydrogen.*—The cause of these anomalous results was indicated by an experiment in which the water to be analysed, contained in a Winchester quart bottle, was allowed to stand in an atmosphere of hydrogen overnight, estimations being made before and after such exposure. The results obtained show, that whilst the volume of hyposulphite solution needed in the evening was 6.32 c.c., a mean of 10 experiments varying between 5.65 and 6.80, the amount required by the same volume of water after standing overnight in hydrogen was only 4.18 c.c., a mean of four experiments varying between 3.8 and 4.5.

*Diffusion the disturbing Influence.*—The conclusion was, that when aerated water is introduced into an atmosphere of pure hydrogen, it immediately begins to lose oxygen by diffusion into the hydrogen until an equilibrium is established, a fact hitherto overlooked by the experimenters with this process.

*Explanation of the previous Experiments.*—This explains the previous observations, viz., that the highest results are obtained when the hyposulphite is added quickly and immediately after the introduction of the water into an atmosphere of hydrogen, because the oxygen is estimated and combined before it has had time to diffuse to any great extent, the slight difference in the time of exposure between a quick and a slow titration being quite sufficient to give a marked loss of oxygen by diffusion during the slower addition of hyposulphite. The variation in the results of the apparently identical experiments first given, being explained by the slightly longer or shorter time taken over each titration, and the consequent greater or less facility for diffusion.

*Results less in proportion to the amount of exposure to Hydrogen.*—This conclusion, that diffusion is the disturbing influence, is borne out by further experiments easily suggested by the preceding.

Six series of estimations were carried out on the same sample of water, and in each succeeding one a slightly longer time of exposure to hydrogen was given. The figures represent the volumes in c.c. of hyposulphite required for one measure of water.

			Mean of 3 experiments.
Series	I.	Titrated immediately and quickly, 6 c.c. of hyposulphite being added at once, the rest carefully drop by drop.....	7.56
..	II.	Titrated immediately, but drop by drop	6.18
..	III.	Titrated drop by drop, after standing 30 seconds in the hydrogen.....	3.72
..	IV.	Titrated as before after standing in a moderate <i>current</i> of hydrogen 1 minute	2.55
..	V.	As in IV, but 2 minutes' exposure ....	1.45
..	VI.	As in IV, but 5 minutes' exposure ....	0.53

It is thus obvious that the result of an oxygen estimation by the present method, depends on the degree of exposure to hydrogen during titration.

*Conditions influencing the Amount of Diffusion.*—The rapidity and amount of the diffusion of dissolved oxygen depend on (1) the surface area of water exposed to hydrogen, influenced by the size and shape of the vessel and the degree of agitation during titration. (2) The volume of the atmosphere of hydrogen. (3) The time of exposure, up to the point of equilibrium (under the Law of Partial Pressures). (4) The volume of water.

*Effect of Size and Shape of Vessel.*—If this be the true explanation of the observed differences, it is clear, that if the water be exposed in a shallow layer to a large volume of hydrogen as in Schützenberger's and Dupré's apparatus, diffusion will take place more quickly than if the water be titrated in a small vessel having a limited surface exposure of the liquid. A series of estimations titrated quickly in a small bottle (200 c.c. capacity) gave 13.56, whilst with the same sample of water titrated quickly in a large flask, using the same hyposulphite, the result was only 9.95, both numbers being the mean of five estimations.

But even in the small bottle a considerable amount of diffusion had taken place, for by modifying the method of procedure\* so as to prevent diffusion, the same water gave 16.6 as compared with 13.56 and 9.95.

The following numbers give the results of this series of observations extended by varying the time of exposure in the large vessel.

\* See description of New Method, page 562.



Series					
I.	II.	III.	IV.	V.	VI.
Small vessel.		Large vessel.			
	Quickly.	Quickly.	1 min.	3 mins.	
—	13.50	10.20	4.20	3.10	—
16.7	13.70	9.90	3.95	2.90	2.7
—	13.60	9.90	4.15	3.00	—
16.5	13.50	9.90	4.20	3.10	2.7
—	13.50	9.85	4.40	3.00	—
16.6	13.56	9.95	4.24	3.02	2.7

In each case, 50 c.c. of water and 10 c.c. of indigo-carmin were used.

- Series I. Maximum result when diffusion is eliminated.  
 „ II. Titrated quickly in small bottle.  
 „ III. Titrated quickly in large flask.  
 „ IV. Titrated after gentle agitation in large flask for 1 minute.  
 „ V. Titrated after gentle agitation in large flask for 3 minutes.  
 „ VI. Minimum readings\* when the diffused oxygen is driven out by a current of hydrogen.

These estimations were repeated the next day with a new and slightly stronger hyposulphite solution, with the following results:—

I.	II.	III.	IV.	V.	VI.	
Small vessel.		Large vessel.				
	Quickly.	Quickly.	1 min.	5 mins.		
13.0	10.5	7.4	3.5	2.0	1.9	
13.0	11.0	7.1	3.9	2.0	1.9	
Means.....	13.0	10.75	7.25	3.7	2.0	1.9

\* The 2.7 c.c. merely represents the combined oxygen in the blue indigo-carmin.

*Percentage of Oxygen diffused under various conditions.*—It is now easy to calculate the percentage of oxygen thus lost by diffusion. In the first place, it is necessary to subtract from the readings the volume of hyposulphite required for the decolorisation of the indigo-carmin used.

The following numbers show that the percentages of oxygen lost agree very closely in the two series :—

*First Series. Diffusible Oxygen*  $16.6 - 2.7 = 13.9$ .

	I.	II.	III.	IV.	V.
Oxygen diffused = 0	3.04	6.65	12.36	13.58	c.c. Hyposulphite.
Percentage.....	0	22	48	89	97 p.c. of total oxygen.

*Second Series. Diffusible Oxygen*  $13.0 - 1.9 = 11.1$ .

	I.	II.	III.	IV.	V.
Oxygen diffused = 0	2.25	5.75	9.3	11.0	c.c. Hyposulphite.
Percentage.....	0	20	52	84	99 p.c. of total oxygen.

Thus we see, that under favourable circumstances, that is, using a small vessel and titrating quickly with least agitation, 20 per cent. of the oxygen diffuses, whilst in a large vessel such as is recommended to be used, 50 per cent. of the oxygen is lost during the titration. The delay of only one minute causing the loss of 90 per cent., whilst in three minutes practically all the oxygen has left the liquid.

*Theoretical Confirmation of amount diffusible.*—This result, viz., that it is possible to lose practically all the oxygen by diffusion is confirmed by the following theoretical consideration.

Supposing the 50 c.c. of water and 10 c.c. of indigo-carmin solution to be fully aerated, and that on introduction into the atmosphere of hydrogen, say 1 litre in volume, all the oxygen diffuses into the gas. Then under the law of Dalton and Henry, the amount of oxygen which could be redissolved by the 60 c.c. of water is calculated as follows :—

1000 c.c. of fully aerated water contains (say) 7 c.c. of oxygen. that is, after contact with an atmosphere containing 20 per cent. of oxygen; 60 c.c. therefore will contain 0.42 c.c. of oxygen. 0.42 c.c. oxygen in 1000 c.c. of hydrogen = 0.042 per cent. of oxygen in the hydrogen. 60 c.c. of water dissolve 0.42 c.c. oxygen in a 20 per cent. atmosphere. What volume will be dissolved in a 0.042 per cent. atmosphere?

$$\frac{0.042 \times 0.42}{20} = 0.0008 \text{ c.c. of oxygen, or}$$

$$\frac{0.0008 \times 100}{0.42} = 0.19 \text{ per cent. of the original gas.}$$

And this is the quantity which would remain dissolved in 60 c.c. of fully aerated water, after exposure in 1 litre of hydrogen until perfect absorptiometric equilibrium was established by diffusion. In other words, the possible loss by diffusion under the above conditions is 99.8 per cent.

Even using a quarter of a litre of water, a loss of 99 per cent. is still possible, in the usual apparatus.

*Reason for the return of the blue colour.*—We are now in a position to understand an observation which the previous experimenters have not failed to note, but which until now has not received a correct explanation. The observation referred to is, that in carrying out the oxygen estimation in the usual manner, the blue colour after having once been destroyed by the hyposulphite almost immediately returns, and if this subsequent coloration be destroyed, the colour will again return, and so on for a long time. The blue colour returns even when the hydrogen used is perfectly freed from all traces of oxygen by passing through the two long tubes filled with beads moistened with the alkaline solution of potassium pyrogallate used in all our experiments.

This observation is at once an indication and a proof of the correctness of our explanation. The previous experiments would lead us to anticipate that the blue colour *would* return, when we remember the great delicacy of the reagent for gaseous oxygen which we possess in the reduced yellow liquid, a mere trace of oxygen being sufficient to cause the change from yellow to blue.

In the ordinary process, the water to be examined is introduced into a large Woullf's bottle containing a little reduced indigo-carmin, which is quite insufficient to combine with all the dissolved oxygen in the water added. We may divide this dissolved oxygen into three portions in an ordinary estimation: (1) a portion oxidises the reduced indigo, and produces the blue colour; (2) part remains dissolved, and combines with the hyposulphite during the titration; (3) the rest diffuses into the hydrogen. When sufficient hyposulphite has been added to produce the first yellow, the diffused oxygen begins to be reabsorbed by the yellow reduced liquid, with formation of the blue compound.

That there is nothing in the reaction between the hyposulphite and indigo-carmin to cause the return of the blue colour can easily be shown.

*No return of the blue colour when free Oxygen is absent.*—If the liquid containing indigo-carmin and also the atmosphere above it are perfectly free from uncombined oxygen, and hyposulphite be added until the blue is turned yellow, no return of the blue colour takes place. The experiments showing this were performed in the apparatus

shown in Fig. 1, p. 561, with 50 c.c. of liquid containing various proportions of indigo-carmin. The water was coloured blue, submitted to a current of pure hydrogen for 10 minutes in each case, and then carefully titrated; the following are the results:—

Aerated* water. c.c.	Indigo- carmin. c.c.	Total. c.c.	Hypsulphite required. c.c.
0	50	50	11·6
25	25	50	5·8 [ $\frac{1}{2}$ of 11·6]
40	10	50	2·35 [ $\frac{1}{3}$ of 11·6]
45	5	50	1·30 [ $\frac{1}{10}$ of 11·6]

(1.) The hypsulphite required was proportional to the amount of colouring matter, within experimental error. (2.) In no case was any blue colour developed, or did any change take place in the appearance of the yellow, although the current of hydrogen was in each case continued for 15 minutes after the yellow colour was produced. In the new method (p. 562) of carrying out the estimation, in which diffusion is entirely prevented, the final yellow liquid has often been kept for an hour in a slow current of hydrogen without the least change of colour towards blue.

*Proof of the Diffusion of dissolved Oxygen into Hydrogen.*—A positive proof that when pure hydrogen comes in contact with aerated water it is contaminated with oxygen, has been obtained as follows:—

A large flask was filled with a fairly strong indigo-carmin solution which was decolorised carefully with hypsulphite. Matters were so arranged that pure hydrogen, freed from all traces of oxygen as before stated, could be passed through aerated water, and thence into the large flask, driving out the sensitive yellow liquid through a tube passing to the bottom of the flask. In this way the hydrogen contaminated with oxygen is imprisoned above a solution which will indicate the presence of oxygen by the formation of a blue colour. This blue colour *was* observed at the surface of the liquid, and after a few minutes it became very intense and unmistakable. Hence the return of the blue colour is proved to be due to the supernatant gas and not to any reaction taking place within the liquid as was supposed by Schützenberger and by Dupré.

*Influence of the amount of Indigo-carmin used.*—These experiments explain a singular observation made by Schützenberger, namely, that by using a small amount of indigo-carmin only half the dissolved oxygen is estimated, when the first decolorisation of the solution is effected; whilst when a much larger quantity of indigo-carmin is

\* The dissolved oxygen contained in this water was entirely lost by diffusion before the liquid was titrated.

employed, *the whole* of the dissolved oxygen is found. The explanation given by him being, that the reaction between reduced indigo and dissolved oxygen is a different one from that taking place between hyposulphite and dissolved oxygen, inasmuch as in the latter reaction, half the oxygen becomes latent as hydroxyl, with subsequent slow liberation of oxygen, whilst in the former no hydroxyl is formed.

His observation, however, will bear another interpretation, namely, if more reduced indigo be present than is sufficient to combine with all the dissolved oxygen contained in the added water, this oxygen is immediately combined by the reduced indigo and its diffusion prevented. Hence *all* the oxygen is obtained. The use of so large a quantity of indigo, however, so disturbs the end-reaction, from the presence of so much of the yellow compound, that "it is difficult to fix the point at which the last trace of blue has been discharged with any degree of accuracy."\*

*Schützenberger's Ratio 1 : 1.*—We will now consider a question on which different experimenters make conflicting statements, namely, the ratio between the first volume of hyposulphite required to give the decolorisation, and the second volume required to give a permanent yellow colour, after all the subsequent returns of colour have been destroyed. Schützenberger† came to the conclusion that for the first decolorisation, "as nearly as possible" half the total volume of hyposulphite is required, and this was afterwards confirmed by Dupré.

*Ramsay and Williams' Ratio 3 : 2.*—Ramsay and Williams (Trans., 1886, 49, 751), however, did not obtain this ratio, but gave another, namely, 3 : 2. But they found a difficulty in obtaining this ratio in all their experiments, and only gave it as a mean expression of the varying ratios they found. Indeed they add, in speaking of this partition of oxygen into two stages of the process: "but it is difficult to devise an equation which will, in a rational manner, account for this partition of oxygen."

Schützenberger's ratio 1 : 1 is exactly what we find‡ when working according to the conditions of his experiments, namely, using a large vessel and a small amount of indigo. Ramsay and Williams' ratio (3 : 2) can easily be explained by the use in their experiments of a smaller titration vessel.

*Infinite range of ratios possible.*—It is evident from the following considerations that this ratio is susceptible of an infinite range of variation.

\* Dupré, *loc. cit.*

† *Fermentation*, by P. Schützenberger.

‡ See III, percentages of oxygen diffused under various conditions, p. 556.

If we ask, in the light of the preceding experiments, on what does this ratio depend? we see that the first reading depends on (1) the amount of indigo-carmin solution, (2) the amount of dissolved oxygen. If we always subtract the volume of hyposulphite required for the oxygen in the indigo-carmin, the rest, " $x$ ," represents the *dissolved* oxygen. The second reading, " $y$ ," represents the *diffused* oxygen (assuming that none is contained in the hydrogen used, that atmospheric air is perfectly excluded, and that none of the diffused oxygen is carried away by a current of hydrogen).

The sum of  $x$  and  $y$  should, theoretically, give a constant result " $c$ ," namely, the total oxygen originally dissolved.

The ratio under consideration is  $x/y$  and  $x + y = c$ .

We have shown that  $x$  may vary enormously, and varies considerably in experiments of which the duration varies but little. Evidently, since  $x$  may fluctuate and  $x + y = c$ ,  $x/y$  cannot be constant or definite. It is, in fact, capable of an infinite range of variation.

Thus—where perfect diffusion had taken place—the ratio would be infinitely small, and where no diffusion had occurred the ratio would be infinitely large.

In other words, in the first case, the first reading would merely represent the indigo-carmin, and the second all the oxygen. In the second case, the first reading would represent both indigo-carmin and oxygen—no second addition of hyposulphite being required.

Hence the ratio may vary in this manner—

Perfect diffusion	$\frac{\text{First reading}}{\text{Second reading}}$	$\overset{*}{0}$	$\overset{*}{2}$	$\overset{*}{4}$	$\overset{\dagger}{5}$	$\overset{\dagger}{6}$	$\overset{\dagger}{8}$	$\overset{\dagger}{10}$	No diffusion.
		$\frac{0}{10}$	$\frac{2}{8}$	$\frac{4}{6}$	$\frac{5}{5}$	$\frac{6}{4}$	$\frac{8}{2}$	$\frac{10}{0}$	

Having proved this source of error in the old method of carrying out the process, the next step is to devise a new one in which the error is eliminated.

The new method must satisfy the following conditions:—

(1.) The aerated water must not at any time expose its *uncombined* oxygen to an atmosphere of hydrogen.

(2.) Precautions must be taken to ensure the use of an atmosphere perfectly free from oxygen, and the apparatus used must not permit any ingress of air.

(3.) When the vessel in which the analysis is made is first filled with water to expel air or to obtain the sensitive yellow liquid, the first portion of gas, having been in contact with aerated water, is contaminated with oxygen and must be entirely driven out.

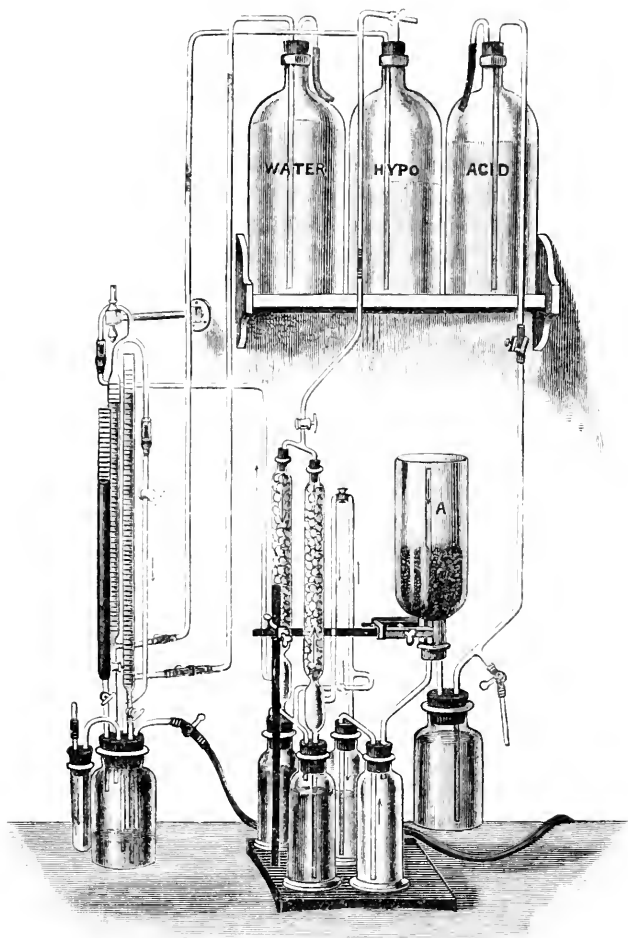
\* Minus the hyposulphite required for the indigo-carmin.

† Schützenberger and Dupré, 1 : 1.

‡ Ramsay and Williams, 3 : 2.

*Apparatus adopted.*—Fig. 1 shows the apparatus adopted by us for carrying out the estimation.

FIG. 1.



It consists essentially (1) of an apparatus for the continuous generation and purification of hydrogen, by the action of dilute sulphuric acid on zinc; (2) a 200 c.c. wide-mouthed bottle fitted with three burettes with glass taps, inlet and outlet tubes for a current of hydrogen, and an outlet tube for the titrated liquid; (3) Winchester stock-bottles of hyposulphite, indigo (not shown), and water, communicating with their respective burettes by glass syphons.

The hydrogen generated in A passes through two wash-bottles containing caustic potash, thence through two Emmerling's tubes filled with glass beads moistened with an alkaline solution of potassium pyrogallate, an arrangement being made whereby the beads may be re-moistened with fresh pyrogallate from the bottles beneath, the liquid being forced up by hydrogen pressure.

Pure hydrogen is supplied continuously (1) to the stock-bottle of hyposulphite, (2) to the hyposulphite burette, and (3) to the titration bottle.

*The New Method.*—A sample of water is examined as follows:—

(1.) 20 c.c. of the water is introduced into the small bottle and about 3 c.c. of indigo solution added.

(2.) A moderate current of hydrogen is passed through the blue liquid by a very fine jet for three minutes to free both water and supernatant gas from free oxygen.

(3.) Hyposulphite is now carefully added, during the flow of hydrogen, until the change from blue to yellow occurs, taking care not to overstep this point.

(4.) A further measured quantity of hyposulphite is now added (say 10 c.c.) sufficient to combine with all the dissolved oxygen in the volume of water, 50—100 c.c., proposed to be used in the estimation.

(5.) The important point now is, that the water is run in from a burette by a capillary tube passing *beneath the surface of the liquid* to the bottom of the vessel. Thus we introduce the water into a liquid which will *at once* combine the free oxygen and thus prevent its diffusion on coming in contact with the hydrogen, the reduced indigo acting as an indicator for the complete oxidation of the hyposulphite. The liquid is kept in constant motion during the addition of the water, which is shut off the moment a permanent blue colour appears.

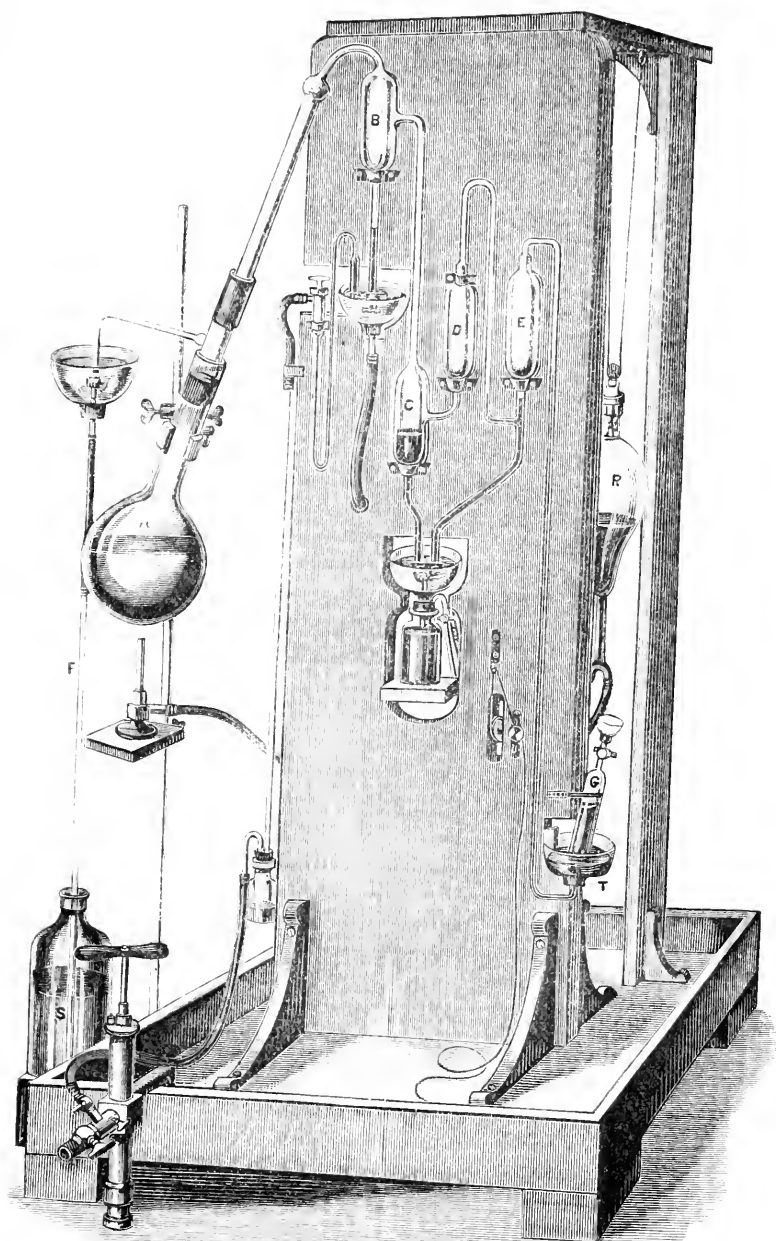
(6.) The blue is decolorised by a further slight addition of hyposulphite. The volume of water used and the total hyposulphite, minus the first addition, are noted and the estimation repeated for confirmation.

When the water contains very little oxygen the second addition of hyposulphite may be omitted, the reduced indigo-carmin being sufficient to take up all the dissolved oxygen. In this case, care must be taken that the oxygen added should require not more than half the hyposulphite first added to decolorise the indigo-carmin.

*Standardisation of the Hyposulphite.*—In order to complete the estimation it is necessary to know the strength of the hyposulphite solution employed. This has entailed a very considerable amount of labour, inasmuch as of the two methods hitherto adopted for this purpose the first was found to be fundamentally wrong, and the second to depend on erroneous data.



FIG. 2.



The first method involves the use of a standard solution of ammonio-cupric sulphate, the second the use of distilled water saturated with air at a known temperature and pressure, using Bunsen's coefficients of absorption to obtain its oxygen value.

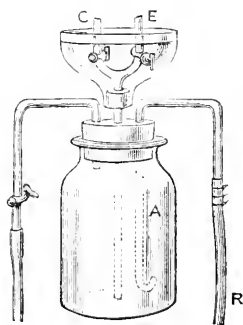
*Re-determination of the Oxygen-value of aerated distilled water.*—The importance of the accuracy of the data employed for the calculation of the oxygen value of distilled water saturated with air, induced us to make independent estimations by boiling out the gases *in vacuo* and subsequently measuring the volume of oxygen.

For this purpose we devised and constructed the apparatus shown in Fig. 2.

At the outset it will easily be understood that an essential in apparatus designed for the boiling out of dissolved gases *in vacuo* is, that there should be no possibility of atmospheric air gaining access to the vacuous interior. India-rubber joints freely exposed to air are inadmissible, because air is capable of diffusing through even thick india-rubber. To secure freedom from such leakage, the apparatus was constructed entirely of glass, with the exception of two tight india-rubber joints which were between glass surfaces and water luted. The glass taps, also, are all submerged in water.

It was found necessary to place an air trap, as shown, beneath C and E to intercept air which was found to leak through the thick india-rubber tubing connecting the mercury reservoir R with the mercury-pump, even though the joints were securely wired. Fig. 3 sufficiently explains how the air was intercepted in A. The apparatus

FIG. 2.



is first completely exhausted of air as follows: About 200 c.c. of distilled water is pumped through the side tube F, into the large bolt-head. The lamp beneath A is lit, and the apparatus exhausted by the air-pump, the water meanwhile boiling and aiding in the expulsion of the air.

To complete the exhaustion the mercury-pump is used.

The three-way tap beneath B is turned to communicate with the mercury reservoir R, mercury rises in B, and, by a suitable turn of the three-way tap, is allowed to flow into the U-tubes, the tap is closed, and thus all communication with the air is shut off.

The boiling is continued, the vapour carrying all the remaining air into D and E, whence it is forced out through the capillary barometer tube and trough T by raising R, and suitably opening the taps beneath C and E. On lowering R a vacuum is produced in E and D, and the last traces of air collected and driven out as before.

When a few minutes' boiling, producing a rush of vapour from C to D, gives no gas on condensing the contents of D and E into the capillary barometer tube, the exhaustion is perfect, and the apparatus ready for the introduction of the water to be examined.

The Winchester quart bottle filled with water is placed so that F passes to the bottom, the tap is opened, and the water rushes in with an immediate escape of part of the gases previously held in solution. When about 2 litres of water have run in, the tap is closed and the heating continued; the gas meanwhile being given off with brisk effervescence, finds its way into the cold chamber E, whence it is driven over and collected in G, a gas tube filled with mercury.

After several exhaustions of E, the water in A boils at a low temperature, and the vapours soon drive all the remaining gas forward into the cool chamber D, where the water condenses and the gas passes forward into E and is driven over as before.

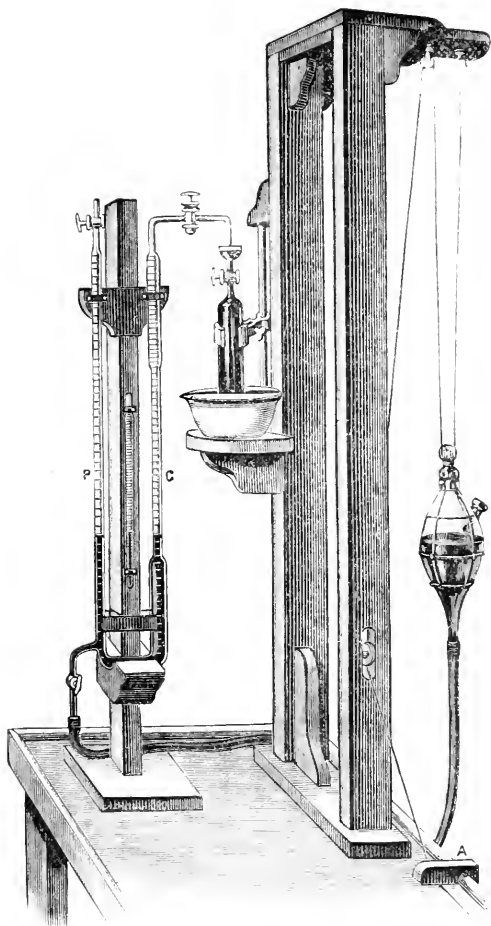
A little practice is necessary to obtain the gas free from water, but this can be accomplished with a little care.

With impure waters, the last portions of gas consist of almost pure carbonic acid, the last traces of which are only expelled on prolonged boiling *in vacuo*. Hence, with distilled water, the exhaustion is perfected much more easily than with waters containing a considerable amount of carbonic acid.

When the gases are completely extracted, it is only necessary to fill up the Winchester quart bottle and measure the volume of water taken for analysis—generally from 1500—2000 c.c.—and to proceed with the analysis of the gases.

The gas tube is removed from the mercury trough T, by introducing a large crucible beneath it. It is transferred to the apparatus shown in Fig. 4, which is a modification of Frankland's gas apparatus, the important point being that the two measurements which require great accuracy are made in the narrow part of the tube G, thus diminishing the experimental error of each reading, namely, (1) nitrogen at the upper part, the wider part at the top being made of sufficient capacity to hold nearly all the nitrogen, (2) nitrogen and

FIG. 4.



oxygen at the lower part. The carbonic acid measurement is made on the lower and wider part of the gas tube.

The tube G joins the collecting tube by a "sealed" tap\* and a ground conical joint fitting into a cup and luted by mercury.

The carbonic acid was absorbed by a 20 per cent. solution of caustic potash, the gas being allowed to stand in the absorption-tube, with its sides wet with the reagent, for half an hour. The oxygen was absorbed by introducing pyrogallie acid to the strong

\* Cetti's patent, avoiding all chance of leakage.

potash solution—the absorption being allowed three-quarters of an hour.

The piece A slides along the side of the table, and by its means the gas can be adjusted to the centimetre marks on G with the greatest nicety.

The pressure, above or below that of the atmosphere—taken at each observation—is read off on the tube P marked in millimetres. The thermometer is also read each time a gas measurement is made, and the apparatus allowed to gain the temperature of the gas-room by standing untouched for a quarter of an hour before each observation. The readings are made by a telescope at the near end of the table, where the gas is also adjusted by moving A backwards or forwards.

*Method of Aeration.*—Before giving the results of the estimations made with distilled water saturated with air, it is necessary to describe the method of aeration.

Freshly distilled water adjusted to the required temperature was aerated by vigorous agitation in two Winchester quart bottles half full of water, the air being renewed five or six times by emptying the contents of one bottle into the other and again dividing into two portions, which were repeatedly agitated with fresh air.

When aerated, one bottle was filled and allowed to stand, stoppered, for half an hour, to an hour to get rid of minute air-bubbles. Then the gases were extracted and analysed, as before described, the barometer having been read to obtain the pressure at which the water was aerated.

The results are calculated from the following formula:—

$$\frac{v_{1, 2, 3} \times [P \pm d \pm c - t]mm \times 273000}{[pa - ta]mm \times T \times V} = x_{1, 2, 3}$$

where  $v$  = volume of gas measured.

$P$  = atmospheric pressure when measured.

$d$  = difference in level of mercury in the two limbs.

$c$  = correction to be applied to adjust the graduation.

$t$  = tension of aqueous vapour at  $T$ .

$pa$  = atmospheric pressure when the water is aerated.

$ta$  = tension of aqueous vapour at temperature of aeration.

$T$  = absolute temperature when gas was measured.

$V$  = volume of water used.

The results are thus found in cubic centimetres of gas, measured at  $0^{\circ}$  C. and 760 mm. bar. dissolved by 1000 c.c. of water aerated at  $t^{\circ}$  C. with a *dry* pressure of 760 mm.

The barometer readings need not be reduced to zero, as this correction would act in two ways counteracting each other.

The above formula is not applicable to a sample of water taken for analysis, in which the actual volume of gas present is required to be found. In this case, 760 must be substituted for  $[pa - ta]$  mm. It was thought best to fix, with as great accuracy as possible, the values at 10°, 15°, 20°, and 25°, by means of several determinations at each temperature, and from these values to calculate the remaining ones.

The following are the numbers obtained. They indicate close agreement between the several experiments at each temperature, and also throughout in the ratio between the oxygen and total oxygen plus nitrogen, a ratio always between 33 and 34 per cent., and evidently not a function of the temperature, as some observers claim it to be.\*

They show a wide discrepancy from Bunsen's numbers, but agree well with Dittmar's determinations.†

*Determinations of Dissolved Gases in fully Aerated Distilled Water.*  
Temperature 10° C. Pressure 760 mm. (dry).

	Nitrogen.	Diff. from mean.	Oxygen.	Diff. from mean.	Total gas.	Percentage of oxygen.
(1) .....	15·45	-0·02	7·84	-0·03	23·29	33·69
(2) .....	15·53	+0·05	7·85	-0·02	23·38	33·58
(3) .....	15·56	+0·09	7·85	-0·02	23·41	33·54
(4) .....	15·43	-0·04	7·92	+0·05	23·35	33·94
(5) .....	15·38	-0·09	7·90	+0·03	23·28	33·96
Mean values..	15·47	—	7·87	—	23·34	33·74

Temperature 15° C. Pressure 760 mm. (dry).

(1) .....	13·81	-0·02	7·11	+0·02	20·92	33·97
(2) .....	13·86	+0·03	7·07	-0·02	20·93	33·76
Mean values..	13·83	—	7·09	—	20·92	33·86

Temperature 20° C. Pressure 760 mm. (dry).

(1) .....	12·74	-0·02	6·42	-0·02	19·16	33·52
(2) .....	12·73	-0·03	6·44	—	19·17	33·60
(3) .....	12·75	-0·01	6·45	+0·01	19·20	33·62
(4) .....	12·81	+0·05	6·45	+0·01	19·26	33·46
Mean values..	12·76	—	6·44	—	19·20	33·55

\* Winkler (*Ber.*, 1888, 2851). † "Challenger" Reports, vol. i, Pt. I, p. 100.

*Temperature 25° C. Pressure 760 mm. (dry).*

	Nitrogen.	Diff. from mean.	Oxygen.	Diff. from mean.	Total gas.	Percentage of oxygen.
(1).....	11·81	+0·03	5·94	+0·03	17·75	33·46
(2).....	11·76	-0·02	5·88	-0·03	17·61	33·34
Mean values..	11·78	—	5·91	—	17·69	33·40

From these results, the following table has been constructed, giving the oxygen values for fully aerated distilled water for each half-degree between 5° C. and 30° C., and for an *observed\** pressure of 760 mm. —

*Oxygen Dissolved by Distilled Water. 5—30° C.*

Temp. C.	e.e. Oxygen N.T.P. per litre Aq.	Diff. for 0·5° C.	Temp. C.	e.e. Oxygen N.T.P. per litre Aq.	Diff. for 0·5° C.
5·0°	8·68	0·10	18·0°	6·54	0·07
5·5	8·58	0·09	18·5	6·47	0·07
6·0	8·49	0·09	19·0	6·40	0·06
6·5	8·40	0·09	19·5	6·34	0·06
7·0	8·31	0·09	20·0	6·28	0·06
7·5	8·22	0·09	20·5	6·22	0·06
8·0	8·13	0·09	21·0	6·16	0·06
8·5	8·04	0·09	21·5	6·10	0·06
9·0	7·95	0·09	22·0	6·04	0·05
9·5	7·86	0·09	22·5	5·99	0·05
10·0	7·77	0·08	23·0	5·94	0·05
10·5	7·68	0·08	23·5	5·89	0·05
11·0	7·60	0·08	24·0	5·84	0·04
11·5	7·52	0·08	24·5	5·80	0·04
12·0	7·44	0·08	25·0	5·76	0·04
12·5	7·36	0·08	25·5	5·72	0·04
13·0	7·28	0·08	26·0	5·68	0·04
13·5	7·20	0·08	26·5	5·64	0·04
14·0	7·12	0·08	27·0	5·60	0·03
14·5	7·04	0·08	27·5	5·57	0·03
15·0	6·96	0·07	28·0	5·54	0·03
15·5	6·89	0·07	28·5	5·51	0·03
16·0	6·82	0·07	29·0	5·48	0·03
16·5	6·75	0·07	29·5	5·45	0·03
17·0	6·68	0·07	30·0	5·43	0·02
17·5	6·61				

\* In this table the results are not calculated for aeration at a *dry* pressure of 760 mm., but for an *observed* barometric pressure of 760 mm. When the observed pressure is *below* 760 mm.  $\frac{1}{760}$ th the value must be *subtracted* for every 10 mm. diff. The same value must be *added* when the pressure is *above* 760 mm.

The following numbers show the variation from Bunsen's figures (hitherto used for the standardisation of the hyposulphite), and the close agreement with Dittmar's determinations:—

Oxygen.				Nitrogen.			
	Found.	Dittmar.	Bunsen.		Found.	Dittmar.	Bunsen.
10° C. ..	7·87	8·00	6·79	10° C. ...	15·47	15·35	12·70
15 ....	7·09	7·20	6·25	15 ..	13·83	13·95	11·67
20 ....	6·44	6·53	5·93	20 ..	12·76	12·79	11·08
25 ....	5·94	5·97	—	25 ..	11·81	11·82	—

From this comparison, we have no hesitation in adopting the values we have obtained, for the standardisation of the hyposulphite solution by aerated distilled water. This method has the advantage of being a titration carried out under almost the same conditions as the examination of a sample of water.

*Indigo Standardisation.*—When once the hyposulphite has been carefully standardised by distilled water, this rather troublesome aeration may be avoided by finding the oxygen-value of the indigo-carmin solution. This solution remaining constant may be used for the subsequent standardisation of the hyposulphite.

It is only necessary to take a suitable quantity of indigo solution, diluted with water if necessary, free it from all dissolved oxygen by a current of pure hydrogen continued for five minutes, then carefully decolorise with hyposulphite, the value of which has been carefully found by using aerated distilled water. The hyposulphite solution slowly loses strength even when kept in hydrogen, and should be standardised daily when required to be used.

*Copper Method of Standardisation.*—We are now in a position to examine the method of standardisation by the use of ammoniacal cupric sulphate. This consists in titrating a standard solution of cupric sulphate containing in 1 litre, 4·462 grams of the hydrated salt precipitated and re-dissolved in ammonia, adding the hyposulphite in an atmosphere of hydrogen until the blue ammoniacal liquid is rendered colourless. 10 c.c. of such a solution are equivalent to 1 c.c. of oxygen, N.T.P.

The method was tested by applying the oxygen-value thus found for the hyposulphite to the examination of fully aerated distilled water at 10°, 15°, and 20°. The results thus found for distilled water are so far removed from the actual values found by extracting the gases *in vacuo*, that we may safely reject this method of standard-



isation as inaccurate. The following are the details of this comparison:—

*Titration of the Copper Solution.*

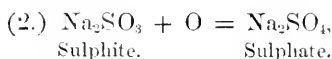
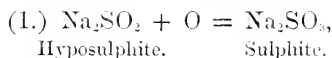
20 c.c. copper solution = 39.40 or 19.70	} Mean 19.76 c.c. hypo- sulphite = 1 c.c. oxygen N.T.P.
39.55      19.77	
39.55      19.77	
39.65      19.82	
39.50      19.75	

*Examination of the Distilled Water.*

Distilled water.	Hypo.	c.c. Oxygen found.	Means.	Another series gave	True value.
10° C... 1000 c.c. = 114.6	112.9 ÷ 19.76 =	5.79	5.71	5.67	7.77
		5.71			
		5.62			
15° C... 1000 c.c. = 100.4	99.5 ÷ 19.76 =	5.08	5.02	5.09	6.97
		5.03			
		4.96			
20° C... 1000 c.c. = 92.6	89.8 ÷ 19.76 =	4.68	4.62	4.65	6.28
		4.54			
		4.66			

The probable causes of the failure of the copper method of standardisation are not far to seek.

In the first place, the copper solution is alkaline, and this, as we shall show, exerts a disturbing influence. In the second place, the reaction occurring when free oxygen is estimated in water, is probably not so simple as has been supposed. The *nascent* sulphite formed no doubt taking up a portion of the free oxygen with formation of sulphate, whilst in the case of the combined oxygen in the cupric solution, this latter reaction does not take place.



Thus the oxygen taking part in reaction (2) is *lost* where the hypo-sulphite solution is standardised by a method in which this latter reaction is unrecognised.

*Comparison of the New Method with the Volume of Gas found.*—We next proceed to apply the volumetric process as thus modified to the examination of samples of water from different sources, and to com-

pare the results with the absolute volume of gas obtained by boiling out the same water *in vacuo*.

The following formula is applicable to the volumetric process  $\frac{d \times h_s \times Od}{s \times hd} = x$  c.c. oxygen per litre of water, where  $d$  and  $s$  = the volumes of distilled water and sample respectively used and  $hd$  and  $h_s$  = hyposulphite required for distilled water, and sample respectively, and  $Od$  the volume of dissolved oxygen (N.T.P) contained in 1 litre of the distilled water used.

The following are the results of this comparison made on five different samples of London tap water collected on five different days. In each case a Winchester quart bottle was filled with the water as drawn from the tap. Three estimations were made by the improved method, and then about 1700 c.c. of the remaining water taken for the gasometric estimation.

*London Tap Waters.*

	(1.)	(2.)	(3.)	(4.)	(5.)
	c.c.	c.c.	c.c.	c.c.	c.c.
Nitrogen.....	13·22	13·95	13·36	13·43	13·49
Oxygen .....	5·15	5·91	5·38	6·31	5·80
Carbonic acid .....	7·98	9·29	6·70	7·35	8·11
Total gas.....	26·35	29·15	25·44	27·09	27·40
Oxygen by the new volumetric method .	5·52	6·13	5·64	6·41	6·24
Gas obtained .....	5·15	5·91	5·38	6·31	5·80
Difference.....	0·37	0·22	0·26	0·10	0·44

Mean difference 0·28 c.c. oxygen per litre of water.

The oxygen values obtained by the two methods show close agreement, considering the possible experimental error in so complex a comparison. The mean difference being only 0·28 c.c. of oxygen per litre of water, showing that the method gives good results with ordinary drinking waters.

The next series of comparisons were made on Thames water collected just below the bridge at Richmond. These, like the tap waters, show that the method is applicable to tolerably pure river water.

The following are the details of the estimations:—

*Thames at Richmond.*

	(1.)	(2.)	(3.)	(4.)
Nitrogen .....	17.14	16.74	13.75	13.11
Oxygen .....	8.37	8.00	5.24	6.06
Carbonic acid .....	7.35	7.18	7.38	7.95
Total gas .....	32.86	31.92	26.37	27.12
Oxygen by the new method	8.95	8.98	5.87	6.13
Gas obtained .....	8.37	8.00	5.24	6.06
Difference .....	0.58	0.98	0.63	0.07

Mean difference, 0.56 c.c. of oxygen per litre of water.

A further comparison was made with very impure Thames water collected at Crossness, opposite the southern outfall for London sewage, 12 miles below London Bridge.

These in like manner indicate that the method gives good results even with an impure water of this character.

The following are the details of the analyses :—

*Thames, opposite Southern Sewage Outfall.*

	(1.)	(2.)	(3.)	(4.)	(5.)	(6.)
Nitrogen .....	17.08	17.58	17.60	17.46	15.96	16.96
Oxygen .....	2.51	0.59	0.13	1.06	4.36	4.68
Carbonic acid .....	14.00	15.29	15.77	14.51	26.18	15.13
Total gas .....	33.59	33.46	33.50	33.03	46.50	36.77
Oxygen by the new method	3.01	0.99	0.34	1.65	5.18	5.94
Gas obtained .....	2.51	0.59	0.13	1.06	4.36	4.68
Difference .....	0.50	0.40	0.21	0.59	0.82	1.26

Mean difference, 0.63 c.c. of oxygen per litre of water.

In sample (5) the low nitrogen is explained by the abnormally high carbonic acid.

The process thus applied to waters of such varied character, and containing such widely different amounts of oxygen, with a mean

difference of only 0.5 c.c. from the value obtained by extracting and measuring the gases, shows that, although perfect accuracy cannot be guaranteed for the process thus improved, yet the results obtained are not far removed from the truth, and certainly give very valuable indications as to the oxymetric condition of samples of water submitted to its operation. Perhaps no other volumetric process satisfies so well the conditions of so difficult a problem as the estimation of dissolved oxygen in water.

In investigations on the action of micro-organisms in the purification or putrefaction of impure waters, it is hoped the process will give valuable aid.

*Influence of Acidity and Alkalinity.*—Although the method is applicable to pure and impure waters, and even to brackish waters, this is not the case if the water contains even small quantities either of free acid or alkali. Thus, if  $\frac{1}{1000}$ th part of sulphuric acid be added to pure water, not only is the oxygen value obtained a different one, but the whole reaction is disturbed. The volume of hyposulphite required for the first decolorisation is greater; this only producing a light, straw-yellow, instead of the fine deep-yellow of a normal titration. The delicacy of the reaction is altogether destroyed, a much larger volume of water than usual only slowly producing a light-blue colour, instead of the distinct coloration produced by even half a cubic centimetre of pure water in a normal titration. Oxalic acid has a similar action. The same proportion of ammonia has an entirely opposite effect. The oxygen value is raised instead of lowered, and the delicacy of the reaction is not impaired, although the colour reaction is very much modified. The results compare as follows:—

	Pure water.	$\frac{1}{1000}$ part of sulphuric acid.	$\frac{1}{1000}$ part of ammonia.
100 c.c. =	28.5	17.3	35.5
	28.7	17.3	36.1
	28.9	—	—
	29.0	17.3	35.8
	28.1	—	—
	Mean 28.6		

Sodium bicarbonate has no effect.

Of course, when other substances than oxygen, which decompose hyposulphite, are present in the water, the accuracy of the method is proportionately disturbed.

*Delicacy of the Reaction.*—With pure water, the change of colour is a very highly sensitive reaction and the most delicate test for the presence of free oxygen we possess, one part of oxygen in two million parts of water being sufficient to bring about a distinct change of colour.

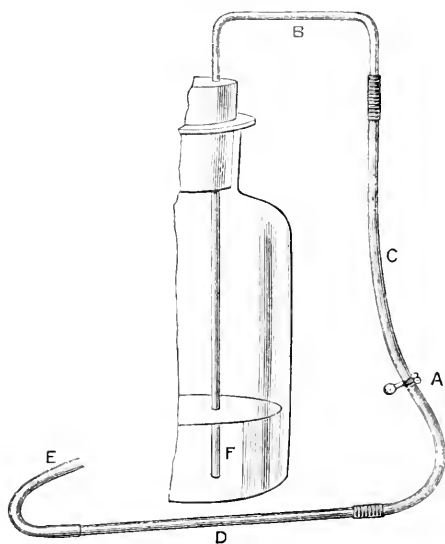
If a quantity of the reduced yellow liquid be sealed up in a vessel containing pure hydrogen, it retains its yellow colour and its power of turning blue when opened and exposed to air, even after many days.

The blue compound obtained by exposing the titrated liquid to air is likewise permanent in pure hydrogen, but it is a curious fact that it slowly fades and turns to yellow on further exposure to air. This is no doubt due to the presence of sulphite, as a crystal of sodium sulphite dropped into a solution of the untitrated indigo-carminc causes the same slow fading of colour, and gives subsequently the same yellow liquid.

This is in strict accordance with the observations made on the action of atmospheric oxygen in the fading of colour in dye-stuffs (*Chem. News*, 39, 313).

*Diffusion of Oxygen through India-rubber.*—The delicacy of this reaction may be employed to show the rapid diffusion of atmospheric air through india-rubber tubing. The experiment is made as follows:—

FIG. 5.



100 c.c. of water and 3 c.c. of indigo-carminc are freed from oxygen and decolorised in the usual way. The liquid is then forced out by hydrogen pressure on opening A.

When the liquid has flowed through B, C, D, E for a few seconds the pinchcock A is closed.

The liquid is seen to be yellow at F, B, and D, and is allowed to remain in the india-rubber tube C for five minutes. If now A be carefully opened so as to allow the former contents of C to be seen in the glass tube D, it will at once be observed that whilst the liquid in F, B, and D had remained unchanged, that in C had turned quite blue from the absorption of atmospheric oxygen diffused through the india-rubber. Even one minute's exposure is sufficient to give an indication.

This experiment has a practical bearing on the construction of the apparatus as figured in Dupré's paper and in Sutton's book, in which the hyposulphite solution is made to pass through several feet of india-rubber tubing before reaching the titration vessel, its strength, of course, diminishing with the time of remaining in contact with the india-rubber.

In the form adopted by us, the hyposulphite is conveyed from the stock bottle to the titration vessel by a *glass* syphon, and only sufficient india-rubber used to accommodate a pinchcock and to make one other connection necessary for the free motion of the titration vessel.

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#### LIV.—*Zinc Dextrosate.*

By ALFRED C. CHAPMAN, Demonstrator of Chemical Technology,  
University College, London.

VARIOUS compounds of dextrose, with the oxides of barium, strontium, calcium, lead, and copper have been described by Péligot, Brendecke, and other chemists, but no compound of dextrose with oxide of zinc appears to have been noticed. When an ammoniacal solution of zinc hydrate is added to a concentrated solution of dextrose in 90 per cent. alcohol, a white, curdy precipitate immediately falls.

4 grams of thoroughly washed zinc hydrate were dissolved in the smallest possible quantity of strong aqueous ammonia, and this was then added to a solution of 5 grams of dextrose in about 400 c.c. of 90 per cent. alcohol. After standing for 12 hours, the clear supernatant liquid was poured off, and the white precipitate transferred to a perforated porcelain plate placed in a funnel and connected with a filter-pump.

After having been thoroughly washed with alcohol, and allowed to drain in a current of air, it was placed under the receiver of an air-

pump and dried to a constant weight in a vacuum over sulphuric acid.

By this method I obtained rather more than 4 grams of the dry zinc dextrosate

*Results of Analysis.*

I.	0.428 gram	gave 0.290 gram $\text{CO}_2$ and 0.178 gram $\text{H}_2\text{O}$ .
II.	0.362	„ 0.248 „ „ 0.149 „
III.	0.500	„ 0.204 gram $\text{ZnO}$ .
IV.	0.482	„ 0.1965 „
V.	0.500	„ 0.205 „

	Calculated for $\text{C}_6\text{H}_{12}\text{O}_6 \cdot 2\text{ZnO} + 3\text{H}_2\text{O}$ .	Found				
		I.	II.	III.	IV.	V.
C. ....	18.19	18.45	18.67	—	—	—
H. ....	4.54	4.60	4.56	—	—	—
Zn. ....	32.83	—	—	32.74	32.71	32.90

This compound, when treated with water, is decomposed into dextrose and zinc oxide. The zinc in Analyses III and V was determined by treating a weighed quantity with water, heating for some time, filtering off the zinc oxide, and weighing. The dextrose in the filtrates was also estimated.

The following are the results:—

	Calculated for $\text{C}_6\text{H}_{12}\text{O}_6 \cdot 2\text{ZnO} + 3\text{H}_2\text{O}$ .	Found.	
		(a.)	(b.)
Dextrose. ....	45.46	45.5	45.9
Zinc oxide. ....	40.91	40.8	41.0
Water. ....	13.63	*13.7	*13.1
	<hr/> 100.00	<hr/> 100.0	<hr/> 100.0

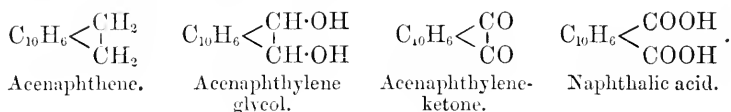
Zinc dextrosate is a white, amorphous substance. It is very hygroscopic and parts with its moisture with very great difficulty. It is insoluble in alcohol, ether, and chloroform, but is easily soluble (probably after decomposition) in dilute acids. When heated, it decomposes, decomposition commencing at a temperature of about  $65^\circ$  to  $70^\circ$ . In one experiment, a solution from which the zinc dextrosate had been separated as above described on standing for several weeks deposited small needle-shaped crystals, but the quantity was far too small for any investigation.

\* The water by difference.

LV.—*Oxidation Products of Acenaphthene.*

By T. EWAN, B.Sc., and J. B. COHEN, Ph.D., Owens College.

THE following series of experiments was undertaken with the view of preparing the intermediate products of the oxidation of acenaphthene and naphthalic acid. According to the present view of the constitution of acenaphthene (Ekstrand, *Ber.*, 1885, 2881, Philip and Bamberger, *Ber.*, 1887, 237), it should yield on oxidation a dialcohol and diketone of the following constitution:—



The present paper contains a preliminary account of these experiments, which are still being carried on.

*Action of Lead Oxide, Lead Nitrate, and Water upon Dibromacenaphthene Bromide, C<sub>12</sub>H<sub>8</sub>Br<sub>2</sub>, Br<sub>4</sub>.*

Dibromacenaphthene bromide was boiled with water and lead oxide for 2 to 3 days with reflux condenser, and the product distilled in a current of steam. A substance passed over which crystallised in brilliant yellow needles. The same compound was obtained on heating the bromide with lead oxide and water at 150°, and also with a solution of lead nitrate. The yield in all cases was so small that any further investigation as to the constitution of the compound has been postponed. The substance was recrystallised from alcohol, and melts at 126—129°. It gave the following results on analysis:—

	Found.	Calculated for C <sub>12</sub> H <sub>4</sub> O <sub>2</sub> Br <sub>2</sub> .
C .....	45.62	46.15
H .....	3.16	2.53
Br .....	46.80	47.06

*Acenaphthylene Glycol Monoacetate.*—A better result was obtained by converting acenaphthylene dibromide into the acetate and decomposing the product with potash.

2 grams of the dibromide are boiled with 2 grams of caustic potash and 7—8 c.c. of glacial acetic acid. In a few minutes potassium bromide begins to separate, and the reaction is soon complete.



The product is neutralised with caustic soda, the buff-coloured precipitate collected and washed with water. The precipitate is dried, and crystallised from light petroleum, and recrystallised from acetic acid or alcohol. It forms long, slender, yellow needles, which melt at  $122\text{--}122.5^\circ$  (uncorr.); it is easily soluble in alcohol, less soluble in methyl alcohol, very soluble in ether and glacial acetic acid. 40 grams of the bromide give 10 grams of product. The substance gave on analysis the following results:—

	Found.	Calculated for $\text{C}_{14}\text{H}_{12}\text{O}_3$ .
C.....	73.65	73.67
H.....	5.7	5.27

The compound is therefore acenaphthylene glycol monoacetate,  

$$\text{C}_{10}\text{H}_6 < \begin{array}{c} \text{CH}\cdot\text{OH} \\ | \\ \text{CH}\cdot\text{O}\cdot\text{C}_2\text{H}_3\text{O} \end{array}$$

*Acenaphthylene Glycol Diacetate*.—The monoacetyl compound was boiled with excess of acetic anhydride for half an hour, and the mass poured into water. When the excess of anhydride was decomposed, a brown solid residue remained, which was collected, washed with water, and crystallised from methyl alcohol. It melts at  $130^\circ$ , and gave on analysis the following results:—

	Found.	Calculated for $\text{C}_{10}\text{H}_6 < \begin{array}{c} \text{CH}\cdot\text{O}\cdot\text{C}_2\text{H}_3\text{O} \\   \\ \text{CH}\cdot\text{O}\cdot\text{C}_2\text{H}_3\text{O} \end{array}$
C.....	70.75	71.11
H.....	5.54	5.20

It is a yellow, crystalline substance.

*Acenaphthylene Glycol*.—1.6 gram of the monacetyl compound and 1 gram of caustic potash are dissolved in methyl alcohol and boiled for 2 to 3 hours on the water-bath. On cooling, long needles separate, which may be recrystallised from methyl alcohol. They are colourless, melt at  $204\text{--}205^\circ$ , and are slightly soluble in cold methyl alcohol or hot water. The substance gave the following results on analysis:—

	Found.	Calculated for $\text{C}_{10}\text{H}_6 < \begin{array}{c} \text{CH}\cdot\text{OH} \\   \\ \text{CH}\cdot\text{OH} \end{array}$
C.....	77.18	77.42
H.....	5.62	5.38

On oxidation with an alkaline 4 per cent. permanganate solution in the cold, a white, crystalline acid is formed, melting at  $266\text{--}267^\circ$ ,

which is doubtless naphthalic acid. No intermediate oxidation product of the glycol could be obtained in this way.

*Acenaphthylene Glycol Monobenzoate*.—1 gram acenaphthylene bromide was dissolved in ether, and 1.44 gram of silver benzoate added. The reaction goes on in the cold. The product was collected and the ether evaporated. The residue may be crystallised from methyl alcohol or toluene, and forms small, colourless plates melting at 189—190°. A second portion dissolved in alcohol was treated with excess of moist silver benzoate, extracted with light petroleum, and recrystallised from glacial acetic acid. The product was the same.

	Found.		Calculated for
	I.	II.	$C_{10}H_6 \begin{matrix} \text{CH}\cdot\text{OH} \\   \\ \text{CH}\cdot\text{O}\cdot\text{C}_7\text{H}_5\text{O} \end{matrix}$
C .....	78.73	78.71	78.62
H .....	5.38	5.04	4.83

*Acenaphthene Ketone*.—To obtain the methyl-derivative of acenaphthylene glycol, we acted on the glycol with methyl iodide and sodium alcoholate. The result turned out very different from what we anticipated. 2 grams of the glycol were mixed with alcohol insufficient for complete solution, and 0.5 gram of sodium, dissolved in about 5 c.c. of absolute alcohol, added. 3.1 grams of methyl iodide were introduced, and the mixture heated for two hours at 150—160°. Sodium iodide separated. The product was diluted with water, extracted with ether, the ethereal solution dehydrated over calcium chloride, and evaporated. The residue solidified, and was recrystallised from alcohol. The substance forms pale yellow needles melting at 119—119.5°. It gave on analysis the following results:—

	Found.	Calculated for
		$C_{12}H_8O$ .
C .....	85.71	85.78
H .....	4.78	5.21

It is not acted on by dry, gaseous hydrochloric acid when passed through its solution in toluene, or when boiled with glacial acetic acid. It combines with phenylhydrazine acetate, but the amount of product obtained was insufficient for analysis. The compound will therefore be a ketone of the following constitution:  $C_{10}H_6 \begin{matrix} \text{CH}_2 \\ | \\ \text{CO} \end{matrix}$ . We

explain the reaction by supposing that the sodium alcoholate has a dehydrating action on the glycol, removing 1 mol. of water.

To prepare the alkyl ethers of acenaphthylene glycol, we had recourse to the action of sodium ethylate on acenaphthylene dibromide, and the results, although they have not yielded the desired

compound, may be of some interest. 2 grams of acenaphthylene bromide, 0.35 gram sodium, and 10 c.c. of alcohol were allowed to stand in the cold for one hour and then heated just to boiling. On cooling, the whole solidified; after crystallisation from alcohol the product was obtained in long needles melting at 94—95°. It gave the following results on analysis:—

	Found.	Calculated for $C_{12}H_{10}$ .
C.....	92.90	93.56
H.....	6.76	6.45

It formed a crystalline compound with picric acid, melting at 161—162°. The substance is, therefore, acenaphthene.

If the acenaphthylene bromide be dissolved in anhydrous benzene, and then heated with dry sodium alcoholate, a brown oil is formed, which readily combines with picric acid to form a yellow, crystalline compound, melting at 201—202°, and gives the following results on analysis:—

	Found.	Calculated for $C_{12}H_8 \cdot C_6H_2(OH)(NO_2)_3$ .
C.....	56.94	56.70
H.....	3.16	2.87

The compound is doubtless the picric acid derivative of acenaphthylene.

We cannot as yet attempt a satisfactory explanation of the course of these reactions, but we intend to investigate them further.

*Tetrabromacenaphthene*.—To obtain the diketone we first prepared the tetrabromo-derivative of acenaphthene.

2 grams of acenaphthylene bromide dissolved in carbon bisulphide and 1.75 gram of bromine, were allowed to stand overnight. Rosettes of crystals separated, which, when pure, melt at 161—162° with decomposition. It is insoluble in alcohol. The following results were obtained on analysis:—

	Found.	Calculated for $C_{12}H_6Br_4$ .
Br .....	67.73	68.08

*Tribromacenaphthene*.—This compound was obtained in one experiment in the preparation of the tetrabromo-derivative; but the conditions were not specially noted at the time, and we have not been able, so far, to obtain it a second time.

It is a yellow crystalline substance, soluble in ether, glacial acetic acid, and hot alcohol. It melts at 88—90°.

It gave the following results on analysis:—

	Found.	Calculated for $C_{12}H_7Br_3$ .
C.....	36.45	36.83
H .....	2.08	1.79

*Action of Chromium Oxychloride upon Acenaphthene.*

To obtain the dialdehyde corresponding to naphthalic acid, we adopted Étard's method. 2 grams of acenaphthene were dissolved in 20 grams of anhydrous carbon bisulphide and 2 grams of  $CrO_2Cl_2$ , dissolved in carbon bisulphide, were slowly added to the cold solution of the acenaphthene. A dark brown, amorphous precipitate was formed, which was filtered through glass-wool, washed with carbon bisulphide, and dried in a vacuum over concentrated sulphuric acid. It was analysed with the following result:—

	Found.	Calculated for $C_{12}H_{10}(CrO_2Cl_2)_2$ .
Cr.....	22.10	22.41

On bringing the compound into water, a green solution is obtained; but the insoluble brown amorphous product obstinately retains chromium, even after prolonged boiling, and in spite of repeated attempts, it was impossible to prepare a pure product. It dissolves also with difficulty in the usual solvents.

To obtain the dialdehyde and diketones of naphthalic acid, we distilled the barium salt of the latter with the lime salt of the fatty acid, and obtained distillates which readily crystallised. The acid chlorides readily react on acenaphthene in presence of aluminium chloride to form well crystallised ketones; but the ketone-group appears to go into the nucleus and not into the ethylene side-chain.

Naphthalimide forms a crystalline chlorine-derivative when acted on by phosphorus pentachloride. The investigation of these compounds will form the subject of a subsequent communication.

LVI.—*Isomeric Change in the Phenol Series.* (Third Notice.)

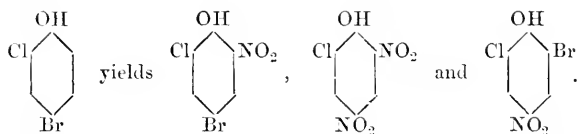
By ARTHUR R. LING.

IN a former communication (Trans., 1887, 147), I have shown that when dibromorthonitrophenol is heated at  $100^{\circ}$  with bromine and water, much bromanil is produced, together with mono- and di-bromoparanitrophenol. The isomeric change which takes place is therefore that of a *parabromorthonitro*-derivative of phenol into an *orthobromoparanitro*-derivative, and this being so, it appeared to me not unlikely that *ortho*chloroparabromorthonitrophenol, a compound which I have already described (Trans., 1887, 791), might also, when similarly heated with bromine and water, undergo isomeric change into *ortho*chlororthobromoparanitrophenol; this seems to be the case, but although I have found that a considerable quantity of chlorotribromoquinone\* and of *ortho*chlorodinitrophenol is at the same time formed, I have obtained no evidence of the production of a mono-halogen derivative of *paranitrophenol*. It having been rendered probable that when chlorine is passed through a hot glacial acetic acid solution of *parabromorthonitrophenol*, the product consists in a great measure of *paranitrophenol*-derivatives, I felt anxious to know whether the isomeric change which appears to occur is, in this case, brought about through the agency of chlorine, or of the bromine which is liberated by the latter. I have to this end, therefore, made several experiments. Firstly, by passing chlorine through a hot glacial acetic acid solution of *orthonitrophenol*; secondly, by heating an acetic acid solution of dichlororthonitrophenol, saturated with chlorine at  $100^{\circ}$ ; and thirdly, by heating dichlororthonitrophenol at  $100^{\circ}$  with chlorine-water. These experiments have, in no case, yielded derivatives of *paranitrophenol*, so that as regards the production of the latter, when chlorine is passed through a hot acetic acid solution of *parabromorthonitrophenol*, it must be due to the liberated bromine.

An interesting, and at first sight rather complicated case of isomeric change takes place, when *ortho*chloroparabromophenol is nitrated by warming it in an acetic acid solution with a slight excess of nitric acid (sp. gr. 1.42), namely, together with the normal products, *ortho*chloroparabromorthonitrophenol and *ortho*chlororthoparadinitrophenol, which are formed in the largest quantity, a not inconsiderable amount of di*ortho*chlorobromoparanitrophenol is also produced. The produc-

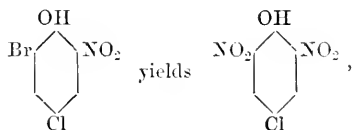
\* I have already shown (Trans., 1887, 790) that when *ortho*chloroparabromorthonitrophenol is heated with bromine and water at  $100^{\circ}$ , the proportions used being  $\text{C}_6\text{H}_2\text{ClBr}(\text{NO}_2) \cdot \text{OH} : 4\text{Br}_2$ , it is entirely converted into chlorobromoquinone.

tion of *ortho*chloro*ortho*paradinitrophenol, and the consequent elimination of bromine renders this case, however, equivalent to the action of bromine on *ortho*chloro*para*bromonitrophenol, the latter being without doubt the initial product of the reaction.

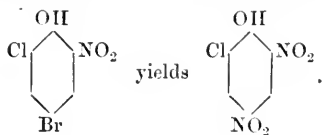


I have also to announce that the isomeric change of *parachlorortho*bromonitrophenol into *ortho*chloro*para*bromonitrophenol, which was pointed out by me (*Trans.*, 1887, 789), does not take place at all, and that a mistake must have arisen in working with impure materials in a manner which I shall explain later, since on re-examining the two isomeric chlorobromo-derivatives of orthonitrophenol, I find that the description which I have given of these compounds needs practically no modification. I am chiefly indebted to Dr. H. E. Armstrong for arousing my suspicions on this point, since my results appeared to be incompatible with some recent investigations made in his laboratory, but on looking into the question more closely, I came to the conclusion that this last-mentioned case of isomeric change is altogether at variance with my other observations; for example, I have shown (*loc. cit.*, 786) that the *para*chlorine-atom in dichloronitrophenol is quite stable when treated with bromine; and it has also been shown by Petersen (*Ber.*, 6, 370), that on heating dichloronitrophenol with nitric acid, the *ortho*chlorine-atom is replaced. From these facts it might be inferred, therefore, that of the compounds *parachlorortho*bromonitrophenol and *ortho*chloro*para*bromonitrophenol, the former modification is the more stable, but the isomeric change of the former into the latter requires the converse of this.

I find, furthermore, that *parachlorortho*bromonitrophenol, when warmed with nitric acid in acetic acid solution, yields *parachlorodithonitrophenol*, thus:—



and that *ortho*chloro*para*bromonitrophenol, when similarly treated, yields *ortho*chloro*ortho*paradinitrophenol, thus:—



*Orthochloroparabromorthonitrophenol.*

This compound is best prepared by nitrating *orthochloroparabromophenol*, the latter being prepared by the chlorination of *parabromophenol* with sulphuryl chloride ( $\text{SO}_2\text{Cl}_2$ ). The melting point of this nitro-compound appears to be somewhat lower than that previously given, namely,  $114^\circ$  instead of  $117^\circ$ . The potassium-derivative,  $\text{C}_6\text{H}_2\text{ClBr}(\text{NO}_2)_2\cdot\text{OK}$ , when not quite pure, or when deposited quickly from supersaturated solutions, crystallises in plates, but on purification may be obtained in beautiful, long, red needles, which are somewhat flat. The calcium salt forms small, red crystals with 7 mols.  $\text{H}_2\text{O}$ , as previously stated.

*Action of Bromine on Orthochloroparabromorthonitrophenol.*

10 grams of *orthochloroparabromorthonitrophenol* was placed in a bottle, together with 40 c.c. of water and 6 grams of bromine (1 mol.), the stopper wired down, and the bottle heated in a bath of boiling water for nine hours. On the following day the bottle was opened, the acid liquid decanted, and the product washed with water. It was then separated from chlorotribromoquinone by extracting with potassium carbonate solution. On purifying the crude brown-coloured salt by recrystallisation and treatment with animal charcoal, it was found that none of the red salt of the *orthonitrophenol*-derivative was present, but that the colour of the salt was yellow. Quite pure salts were not obtained, but the analytical numbers from them, and the melting points of the phenols, leave no doubt that the product consisted of the potassium-derivatives of *orthochlorodinitrophenol*, and *orthochlororthobromoparanitrophenol*.

*No. I Salt.*

0.1627 gram lost 0.0111 gram at  $120^\circ$ , and gave 0.0471 gram  $\text{K}_2\text{SO}_4$ .

	Theory. $\text{C}_6\text{H}_2\text{Cl}(\text{NO}_2)_2\cdot\text{OK}, \text{H}_2\text{O}$ .	Found.
$\text{H}_2\text{O}$ .....	6.55 p. c.	6.82 p. c.
K.....	14.20 „	12.96 „

The phenol obtained from the foregoing melted at  $105\text{--}107^\circ$ ; *orthochlorodinitrophenol* melts at  $110^\circ$ .

*No. II Salt.*

0.1982 gram lost 0.0114 gram at 125° and gave 0.0547 gram  $K_2SO_4$ .

	Theory. $C_6H_2ClBr(NO_2) \cdot OK, H_2O$ .	Found.
$H_2O$ .....	5.83 p. c.	5.75 p. c.
K.....	12.64 „	12.36 „

The phenol from this salt did not show any very definite melting point; it softened at 110°, and melted at 120–130°, decomposing a few degrees above this; *ortho*chloro*ortho*bromo*para*nitrophenol melts at 137° with decomposition.

*Action of Chlorine on Parabromonitrophenol.*

A boiling acetic acid solution of parabromonitrophenol was saturated with chlorine, and allowed to cool. The product was converted into potassium salt, which was orange-yellow, and was not further examined.

*Action of Chlorine on Orthonitrophenol.*

Chlorine was passed into a hot acetic acid solution of *ortho*nitrophenol. On converting the product into potassium salt, it was found to consist solely of *ortho*nitrophenol-derivative, the last portions of the mother-liquor being carefully evaporated and examined under the microscope.

*Action of Chlorine on Dichloronitrophenol.*

These experiments have led to no positive result as regards isomeric change, but it may be well to give them in detail, in order that they may appear final.

I. 10 grams of dichloronitrophenol was dissolved in 100 c.c. of glacial acetic acid, and the boiling solution saturated with chlorine; after standing some time, the solution, from which brilliant scales of chloranil had deposited, was divided, half was poured into water, and the precipitated compound converted into potassium salt, whilst the other half was again saturated with chlorine, placed in a bottle with the stopper wired down, and heated in a water-bath at 100° for three hours: it was then filtered from chloranil, thrown into water, and converted into potassium salt. Nothing but unaltered compound was obtained from either portion.

II. 10 grams of dichloronitrophenol was suspended in 50 c.c.



of chlorine-water, and heated in a bottle at  $100^{\circ}$  for seven hours. On testing a portion of the product, it was found to consist of unaltered substance. The aqueous liquid was then removed at the pump, and the substance transferred to a larger bottle, 300 c.c. chlorine-water added, and then heated at  $100^{\circ}$ , as usual, for six hours. On opening the bottle, it was found that there was considerable pressure; oxides of nitrogen were given off, and there was a strong odour of chloropierin. The portion soluble in potassium carbonate solution consisted, however, entirely of unaltered dichlorororthonitrophenol salt.

### *Nitration of Orthochloroparabromophenol.*

Orthochloroparabromophenol was prepared as stated in a previous portion of the paper by chlorinating *parabromophenol* with  $\text{SO}_2\text{Cl}_2$ ; the parabromophenol employed was pure, but the chlorination product was not examined, further than it was found to consist of colourless needles. The experiment to be described was carried out as follows: 38 grams of pure parabromophenol was fused in a flask, and after cooling somewhat, but not to the solidifying point, 29 grams of  $\text{SO}_2\text{Cl}_2$  was slowly run in with constant shaking. It was then allowed to stand, after which it was first freed from acid, and afterwards dissolved in about 200 c.c. glacial acetic acid, and the solution warmed with a slight excess of nitric acid (sp. gr. 1.42). After standing, it was thrown into water, and the precipitated nitro-compound filtered off at once: when dry it weighed 35 grams. From the mother-liquor, a further quantity of nitro-compound precipitated on standing, which was found to give a yellow potassium salt; the latter, on recrystallisation, was obtained in long, yellow needles. Analysis:—

0.2076 gram lost 0.0126 gram at  $120^{\circ}$  and gave 0.0612 gram  $\text{K}_2\text{SO}_4$ .

	Theory.	Found.
	$\text{C}_6\text{H}_2\text{ClBr}(\text{NO}_2) \cdot \text{OK}, \text{H}_2\text{O}$ .	
$\text{H}_2\text{O}$ .....	5.83 p. c.	6.06 p. c.
K.....	12.64 „	13.19 „

From the above numbers as well as from the melting point of the phenol,  $137^{\circ}$  with decomposition, there is no doubt whatever that this compound was potassium chlorobromoparanitrophenol (compare this vol., p. 57).

The main portion, which was also converted into potassium salt, was found to consist chiefly of orthochloroparabromorthonitrophenol melting at  $114^{\circ}$ , but orthochlorodinitrophenol melting at  $110^{\circ}$  was also separated. The following are the analytical results:—

*Potassium Orthochloroparabromorthonitrophenol.*

- I. 0.2319 gram dried at 100° gave 0.0717 gram  $K_2SO_4$ .  
 II. 0.1963           "           "           0.0598           "

	Theory. $C_6H_2ClBr(NO_2) \cdot OK$ .	Found.	
		I.	II.
K .....	13.42 p. c.	13.84	13.64 p. c.

*Potassium Orthochlorodinitrophenol.*

0.2746 gram lost 0.0150 gram at 130° and gave 0.0870 gram  $K_2SO_4$ .

	Theory. $C_6H_2Cl(NO_2)_2 \cdot OK, H_2O$ .	Found.
$H_2O$ .....	6.55 p. c.	5.46 p. c.
K .....	14.20 "	14.20 "

*Action of Bromine on Parachlororthonitrophenol (correction).*

In my former work the mistake to which I have already alluded must have occurred somewhat in the following manner:—The first portions of *parachlororthonitrophenol* which I used I took the trouble to thoroughly purify by conversion into a salt and recrystallisation (*loc. cit.*, 787), but, in some of the subsequent experiments, I made use of a nitro-compound, which had been obtained from crude monochlorophenol, and which was consequently contaminated with orthochlorophenol, and it would seem that in the experiments in which I decided that isomeric change had taken place, the chloronitro-compound must have consisted almost entirely of *ortho*chloro*ortho*-nitrophenol, since the substance I obtained by the action of bromine at a high temperature undoubtedly consisted chiefly of *ortho*chloro-*parabromorthonitrophenol*.

In repeating this work, 10 grams of *parachlororthonitrophenol*, which had been very carefully prepared from solid *parachlorophenol* and had the correct melting point 87°, was dissolved in glacial acetic acid, and the solution heated to boiling; 9.5 grams of bromine (1 mol.) was then weighed out and slowly added to the solution; when half the bromine had been run in, the solution was again heated to boiling, and the remainder of the bromine added slowly as before; after the addition of all the bromine, the mixture was again heated, and finally allowed to cool and poured into a large bulk of water. The crude substance, after crystallisation from spirit, melted at 123–124°. On conversion into potassium salt, the latter was first of

all obtained in dark-coloured plates, but these on recrystallisation from water had the form of delicate red needles, which gave on analysis  $K = 13.67$  per cent.—theory requires  $13.43$  per cent.—and on decomposition with acid, a nitro-compound, which, when crystallised from spirit, melted at  $125^\circ$  (compare this vol., p. 60).

The calcium salt was obtained in small, dark-red, glistening plates. Analysis:—

- I. 0.3646 gram lost 0.0424 gram at  $100-180^\circ$ , and gave 0.0789 gram  $\text{CaSO}_4$ .  
 II. 0.3555 gram gave 0.0765 gram  $\text{CaSO}_4$ .  
 III. 0.2667 „ 0.2869 silver precipitate.  
 IV. 0.3020 „ 0.3245 „

Theory.		Found.			
$[\text{C}_6\text{H}_2\text{ClBr}(\text{NO}_2)_2\cdot\text{O}]_2\text{Ca}, 4\text{H}_2\text{O}$ .		I.	II.	III.	IV.
$\text{H}_2\text{O}$ .....	11.70 p. c.	11.63	—	—	—
$\text{Ca}$ .....	6.50 „	6.36	6.33	—	—
$\text{Cl}$ } .....	37.56 „	—	—	37.55	37.39
$\text{Br}$ }					

The various specimens of this calcium salt which gave these analytical numbers were obtained from different portions of a solution, so that there is no doubt as to the homogeneity of the same. On decomposing a portion with acid, and crystallising the resulting compound from spirit, it was found to melt at  $125^\circ$ .

#### *Nitration of Parachlororthobromorthonitrophenol.*

In order that the constitution of the foregoing compound might be further confirmed, 4 grams of the crude substance, m. p.  $123-124^\circ$  (see above), was dissolved in hot glacial acetic acid, and a slight excess of nitric acid (sp. gr. 1.42) added. The solution was again heated to boiling. On cooling, needle-shaped crystals separated. The compound was converted into the potassium salt, which, after recrystallisation from water, was obtained in long, lightish-red needles. Analysis:—

0.2162 gram dried at  $100^\circ$  gave 0.074 gram  $\text{K}_2\text{SO}_4$ .

Theory.		Found.
$\text{C}_6\text{H}_2\text{Cl}(\text{NO}_2)_2\cdot\text{OK}$ .		
K .....	15.20 p. c.	15.31 p. c.

On decomposition with acid, a nitro-compound was obtained which melted at  $78-79^\circ$ . The melting point of *parachlorodinitrophenol* is  $80.5^\circ$ .

The constitution of the compound obtained by brominating *para*-chloror*ortho*nitrophenol at a high temperature is, therefore, *parachlor-orthobromor*thonitrophenol, or, in other words, it is a normal product.

*Nitration of Parabromor*thochloror*ortho*nitrophenol.

This substance was nitrated in a manner similar to the foregoing isomeride. The potassium salt of the product was obtained in bright yellow needles. Analysis:—

0.2312 gram lost 0.0153 gram at 120° and gave 0.0736 gram  $K_2SO_4$ .

	Theory. $C_3H_2Cl(NO_2)_2 \cdot OK, H_2O$ .	Found.
$H_2O$ .....	6.55 p. c.	6.61 p. c.
K .....	14.20 „	14.23 „

The phenol from this melted at 110°, which is the correct melting point for *orthochloror*thoparadinitrophenol.

My experiments serve to show that there is a tendency for bromoderivatives of *ortho*nitrophenol to be converted into those of *para*-nitrophenol when heated with bromine and water, although they throw no light on the exact manner in which the change takes place. It might appear that the production of *para*quinone-derivatives from those of *ortho*nitrophenol necessitated the transference of the  $NO_2$ -group from the *ortho*- to the *para*-position, but this view is excluded by the fact that whereas dichloror*ortho*nitrophenol is readily converted into a *para*quinone-derivative when heated with bromine and water, dichloro*para*phenol is certainly not produced in the reaction.

LVII.—*Benzyl-derivatives of the Phenylenediamines.*

By RAPHAEL MELDOLA, F.R.S., and J. H. COSTE.

In a paper published last year by one of the authors and E. H. R. Salmon (Trans., 1888, 774) it was shown that *para*- and *meta*-nitraniline could be readily benzylated by heating with benzyl chloride in the presence of aqueous caustic soda solution. As the benzyl-derivatives of the corresponding diamines have not hitherto received much attention, we have thought it desirable to prepare these compounds and some of their derivatives in order to study the effect produced upon the properties of these derivatives by the presence in

the molecule of a heavy positive radicle such as benzyl. Dibenzyl-paraphenylenediamine has been described in a paper published by Matzudaira (*Ber.*, 1887, 1614).

#### BENZYLPARAPHENYLENEDIAMINE.

Benzylparanitraniline was reduced by boiling the alcoholic solution with tin and hydrochloric acid; the alcohol was distilled off and the tin precipitated by sulphuretted hydrogen. On evaporating the solution, white, scaly crystals separated out, and after purification by dissolving in water, filtering, and again evaporating in the presence of excess of hydrochloric acid, the salt was obtained in the form of lustrous, white scales which proved to be the dihydrochloride:—

0.1528 gram burnt with lime gave 0.1639 gram AgCl.

0.1135 gram gave 9.7 c.c. moist N at 9° C. and 764.3 mm. bar.

Calculated for		
$C_6H_4 < \begin{smallmatrix} NH \cdot C_7H_7 \cdot 2HCl \\ NH_2 \end{smallmatrix}$		
Cl .....	26.19	Found. 26.35
N .....	10.33	10.33

The dihydrochloride is readily soluble in hot and cold water, and is thrown out in the crystalline form by the addition of hydrochloric acid. The salt is almost insoluble in cold alcohol. The aqueous solution, not containing an excess of acid, has the following properties:—

Ferric chloride produces a green colour at first but this soon changes into red, the latter colour becoming more pronounced on heating the solution and an odour of benzaldehyde being at the same time evolved. Potassium chromate produces a deep bluish-green precipitate which on boiling becomes red and gives off benzaldehyde. Bromine-water produces a green colour which changes to red on standing. When the solution is saturated with sulphuretted hydrogen, the addition of ferric chloride causes a blue precipitate of a colouring matter belonging to the methylene-blue group.

The free base is precipitated on adding alkali to the aqueous solution of the dihydrochloride in the form of an ochreous precipitate, which under the microscope is seen to consist of an emulsion of oily globules. On extracting the oil by agitating with ether, and allowing the ethereal solution to evaporate, the base separates as an oil which solidifies to a crystalline mass on standing for some hours. The crystals consist of moss-like aggregations having a melting point of 30°. The base soon becomes red by oxidation on exposure to the air.

*Diacetyl-derivative.*

The dry dihydrochloride was suspended in glacial acetic acid, dry sodium acetate added, and the mixture boiled for about half an hour with the addition of acetic anhydride. On diluting with water and nearly neutralising with ammonia, a whitish, resinous substance separates out. The latter is readily soluble in boiling alcohol, and separates from the saturated solution on cooling in the form of a viscous resin which solidifies to a crystalline cake on standing for some days. The substance crystallises from dilute alcohol in the form of colourless, hexagonal prisms with oblique ends having a melting point of 116·5—117°. Analysis showed that the compound was the diacetyl-derivative.

0·1015 gram gave 0·2680 gram CO<sub>2</sub> and 0·0612 gram H<sub>2</sub>O.

0·1080 gram gave 9·1 c.c. moist N at 10·5° C. and 764 mm. bar.

Calculated for $\text{C}_6\text{H}_4 \begin{matrix} \text{N}(\text{C}_2\text{H}_5) \cdot \text{C}_2\text{H}_5\text{O} \\ \text{NH} \cdot \text{C}_2\text{H}_5\text{O} \end{matrix}$		
		Found.
C .....	72·34	72·01
H .....	6·38	6·70
N .....	9·92	10·12

*Dibenzoyl-derivative.*

Some of the dry dihydrochloride was boiled for about an hour with benzoyl chloride and anhydrous sodium benzoate. The product was washed repeatedly with hot water and finally with dilute ammonia, and then dissolved in hot dilute alcohol and the solution allowed to cool. The substance separates out as an oil which on standing for some days solidifies to a crystalline cake consisting of aggregations of white needles having a melting point of 124°.

0·1033 gram gave 0·3008 gram CO<sub>2</sub> and 0·0522 gram H<sub>2</sub>O.

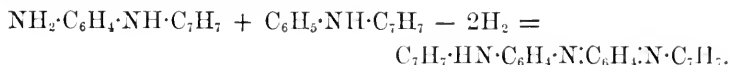
0·1532 gram gave 8·7 c.c. moist N at 12·5° C. and 755·5 mm. bar.

Calculated for $\text{C}_6\text{H}_4 \begin{matrix} \text{N}(\text{C}_7\text{H}_7) \cdot \text{C}_7\text{H}_5\text{O} \\ \text{NH} \cdot \text{C}_7\text{H}_5\text{O} \end{matrix}$		
		Found.
C .....	79·80	79·42
H .....	5·42	5·61
N .....	6·90	6·69

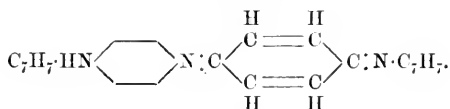
*Oxidation of Benzylparaphenylenediamine in the presence of other aromatic Amines.*

It is well known that by the oxidation of paradiamines in the presence of other amines, certain unstable colouring matters belonging

to the group of indamines are obtained. In order to prepare a dibenzylated indamine, equal molecular proportions of the crystallised benzylparaphenylenediamine dihydrochloride and benzylaniline hydrochloride were dissolved in water, and the necessary quantity of a solution of potassium dichromate gradually stirred into the well-cooled and dilute solution of the bases. The addition of the oxidising agent causes the separation of an intense greenish-blue colouring matter, which is no doubt the dibenzylated indamine formed according to the well-known reaction:—



The constitution of this indamine would be—



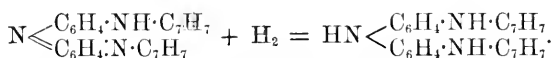
The presence of the benzyl-groups does not appear to confer increased stability upon the colouring matter, which at first collects into a resinous mass of an intense coppery lustre and then rapidly disintegrates, at the same time losing colour and passing almost entirely into solution. A strong odour of benzaldehyde is perceptible from the beginning of the oxidation of the mixed bases. After being allowed to stand for some time in the cold, the solution is filtered to remove a small quantity of some insoluble resinous impurity, and the basic substance dissolved in the solution thrown out (mixed with chromic hydroxide) by means of ammonia. The greenish precipitate is collected, washed with cold water, allowed to drain, and then extracted with boiling alcohol and filtered. The filtrate on cooling deposits a basic substance crystallising in ochreous scales melting at 149—151°. A specimen of this base was analysed with the following results:—

0.1067 gram gave 0.3235 gram CO<sub>2</sub> and 0.0613 gram H<sub>2</sub>O.

0.0885 gram gave 8.7 c.c. moist N at 14° C. and 759.3 mm. bar.

The base is readily soluble in boiling benzene and less soluble in petroleum. It dissolves in dilute hydrochloric acid on warming, but always leaves a small quantity of resinous residue and gives off an odour of benzaldehyde under this treatment. The solution of the hydrochloride gives a greenish-blue colouring matter on oxidation with ferric chloride, but we have not yet been able to ascertain whether this is identical with the original indamine or not. The most obvious view with respect to the constitution of this base is that

it is dibenzylidiamidodiphenylamine, but we have satisfied ourselves that this is not the case by preparing some of the indamine in the manner described and then immediately reducing it by means of zinc-dust and acetic acid. The decolorised solution, after this treatment, was filtered, precipitated by sodium carbonate, and the precipitate collected, washed, and extracted with boiling alcohol as before. The alcoholic filtrate deposited no crystals on cooling, and on distilling off the solvent, an oily base was obtained which did not solidify on long standing and which could be readily oxidised back into a greenish-blue colouring matter very similar to if not identical with the original indamine. This oily base is no doubt dibenzylidiamidodiphenylamine formed from the indamine in accordance with the reaction:—



The oily base on acetylation gave an acetyl-derivative crystallising in white needles melting at  $180^\circ$ , but the quantity obtained was too small for analysis.

A more extended series of experiments will be necessary, in order to determine the nature of the base resulting from the spontaneous decomposition of the dibenzylindamine. We have already made several preparations, and have arrived at certain conclusions, which we think it desirable to make known at the present stage of the work, as the investigation cannot be resumed for some time to come. The fact that the substance is not dibenzylidiamidodiphenylamine, considered with the circumstance that benzaldehyde is given off during the reaction, appears to indicate that the compound is a condensation product, or a mixture of such products derived from benzaldehyde. On this view, the most probable formula is that which represents the substance as a benzylbenzylidene-, or as a dibenzylidene-diamidodiphenylamine. The analytical results do not enable us to decide between these two substances, and, in fact, we are disposed to believe that both of them may be formed by the spontaneous decomposition of the indamine:—

	Calculated for $\text{NH} \begin{smallmatrix} \text{<} \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{CH} \cdot \text{C}_6\text{H}_5 \\ \text{<} \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_5 \end{smallmatrix}$	Calculated for $\text{NH} \begin{smallmatrix} \text{<} \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{CH} \cdot \text{C}_6\text{H}_5 \\ \text{<} \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{CH} \cdot \text{C}_6\text{H}_5 \end{smallmatrix}$	Found.
C .....	82.76	83.20	82.69
H .....	6.10	5.60	6.38
N .....	11.14	11.20	11.55

In the course of further experiments, we always obtained a crystalline basic compound similar in properties to that just described (m. p.  $149$ — $151^\circ$ ), but certain wide discrepancies in the melting



points of different preparations have led to the conclusion that the base is really a mixture of the two compounds formulated above. It will be seen that these two substances differ only by two atoms of hydrogen. By crystallising a specimen from benzene, we obtained a first crop of crystals melting at  $176^{\circ}$ . On adding petroleum to the mother-liquor a second crop was obtained, the melting point of which was  $168-170^{\circ}$ , and by allowing the filtrate to evaporate in a dish a third crop was obtained, of which the melting point was  $149-154^{\circ}$ . These three fractions differed but little in appearance and properties beyond the differences in solubility and melting point. They all contained about the same quantity of nitrogen:—

- 1st crop. 0.0781 gram gave 7.9 c.c. moist N at  $20^{\circ}$  C. and 756.3 mm. bar = 11.51 per cent.  
2nd crop. 0.0647 gram gave 6.1 c.c. moist N at  $18.5^{\circ}$  C. and 756.7 mm. bar = 11.06 per cent.  
3rd crop. 0.0531 gram gave 5.2 c.c. moist N at  $18.5^{\circ}$  C. and 758 mm. bar = 11.28 per cent.

Which of these fractions represents the dibenzylidene-derivative and which the benzylbenzylidene-compound must for the present remain undecided. It would appear most probable that the first fraction having the higher melting point is the dibenzylidene-derivative, but this question can only be settled by a study of the action of benzaldehyde on paradiamndodiphenylamine, and a comparison of the products thus obtained with those described above.

By oxidising equal molecular proportions of the benzyl-diamine and aniline (both in the form of hydrochlorides) with the calculated quantity of potassium dichromate, a greenish-blue indamine is formed, which in the course of about half an hour loses its colour and decomposes with the evolution of benzaldehyde. Nothing definite has, however, been isolated from the products of decomposition. A red colouring matter was found among the latter, which doubtless belongs to the azines.

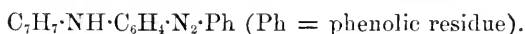
A benzylated saffranine was prepared in the following way. One molecular proportion of benzylparaphenylenediamine, one molecular proportion of benzyaniline, and one molecular proportion of aniline were dissolved in the form of hydrochlorides in boiling water, and oxidised in the usual way by adding a solution containing the calculated quantity of potassium dichromate.\* The hot solution was

\* In the abstract of this paper which appears in the Proceedings (No. 71, p. 116), there is an error which I may take the present opportunity of correcting. It is there stated that one molecule of the benzyl-diamine and two molecules of benzyaniline give a saffranine when oxidised together. This, however, is not the case; the above statement is the actual record of the experiment.—R. M.

filtered as soon as the reaction was complete, and the colouring matter thrown out by the addition of common salt. The saffranine thus formed presented no characters of special interest, and its investigation was not pursued in detail. The red aqueous solution of the chloride becomes blue on adding excess of hydrochloric acid; the alcoholic solution of the colouring matter is violet, with a reddish fluorescence which is not destroyed by ammonia.

*Diazo- and Azo-derivatives of Benzylparaphenylenediamine.*

The free amido-group of the benzyl-diamine is readily diazotised by treating the solution of the hydrochloride with sodium nitrite in the usual way. The solution of the diazo-chloride thus formed is always rendered turbid by the presence of a small quantity of some ochreous precipitate which is simultaneously produced by the action of the nitrous acid. After filtration, the clear solution shows all the characters of a solution containing a diazo-salt. Platinum tetrachloride produces a copious precipitate of an ochreous colour, showing under the microscope no trace of crystalline structure. The analyses of a specimen of this platinum salt, dried under a desiccator in a vacuum, gave numbers which could not be made to agree with any formula, and we are inclined to believe that the platinic salt acts partly as an oxidiser, contaminating the product with oxidised impurities. The solution of the diazo-chloride reacts with phenols in alkaline solution, forming azo-compounds of the type—



Of these compounds we have prepared and examined those formed from  $\alpha$ - and  $\beta$ -naphthol.

*Benzylamidobenzeneazo- $\alpha$ -naphthol.*—On mixing a solution of the diazotised diamine with an alkaline solution of  $\alpha$ -naphthol nothing separates out, but the liquid acquires a deep red colour owing to the formation of the azo-compound,  $\text{C}_7\text{H}_7\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}(\alpha)$ . The latter separates from the alkaline solution on the addition of acid, as a dark, uncrystallisable resin. This azo-compound dissolves in alcohol with an orange colour becoming red on the addition of alkali; it dissolves freely with a red colour in aqueous alkali, and in strong sulphuric acid with a violet colour, becoming redder, and finally precipitating on dilution.

*Benzylamidobenzeneazo- $\beta$ -naphthol.*—The addition of the diazo-chloride solution to the  $\beta$ -naphthol dissolved in caustic soda causes the precipitation of a reddish-brown azo-compound, which, after being collected, washed, and dried, forms a resinous mass having a slight metallic lustre. The substance dissolves but slightly in alcohol

or benzene, but more freely in chloroform, the solution being of an intense orange-brown colour. By adding alcohol to the chloroform solution and allowing the solvents to evaporate slowly, the substance was obtained as a crust of small, warty crystals, having a greenish metallic lustre and melting at about  $124^{\circ}$ . The melting point was not changed after a second crystallisation from chloroform and alcohol.

0.1046 gram gave 10.7 c.c. moist N at  $14^{\circ}$  C. and 764.5 mm. bar.

	Calculated for	Found.
	$C_7H_7 \cdot NH \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot OH(\beta)$ .	
N .....	11.89	12.10

This azo-compound dissolves in strong sulphuric acid with a magenta-red colour, which becomes more orange on dilution, the substance being finally precipitated in an unaltered state.

#### BENZYLMETAPHENYLENEDIAMINE.

This substance was prepared by the reduction of benzylmetanitraniline in precisely the same way as the corresponding paradiamine. After removing the tin as sulphide, the solution was evaporated, and a dense, brownish crystalline deposit of the dihydrochloride was obtained. The crystals appear to consist of rhombohedra built up of laminae. By allowing a drop of the solution to evaporate on a watch-glass, the crystals were seen under the microscope to consist of elongated hexagonal tablets.

0.1685 gram gave 0.1754 gram AgCl.

	Calculated for	Found.
	$C_6H_4 \begin{smallmatrix} NH \cdot C_7H_7 \cdot 2HCl \\ NH_2 \end{smallmatrix}$ .	
Cl .....	26.19	25.76

The free base is an oil which does not solidify on long standing. The aqueous solution of the dihydrochloride gives with ferric chloride a red colour, which changes into orange-brown on standing; the colour at first becomes deeper on heating, and a whitish product of oxidation then separates. The addition of potassium dichromate causes an immediate precipitation of the whitish product of oxidation. Platonic chloride also acts as an oxidiser, giving a dark, amorphous precipitate containing platinum. Sodium nitrite gives a reddish-brown precipitate, which appears to consist of a mixture of an azo- and a diazo-compound. This was shown by the decomposition of the substance with the evolution of nitrogen during an attempt to obtain a pure specimen by crystallisation from alcohol. The diacetyl-deri-

ivative of the diamine was prepared by heating some of the dihydrochloride with acetic acid, dry sodium acetate, and acetic anhydride; it proved to be an uncrystallisable, resinous substance.

*Dibenzoyl-derivative.*

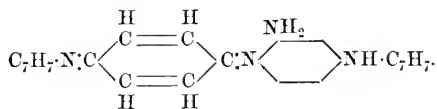
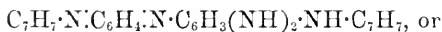
This compound was prepared by heating the dihydrochloride with benzoyl chloride and dry powdered sodium benzoate in a flask at the temperature of boiling water. If this temperature is exceeded, the reaction takes a different course, and resinous products are formed. The benzoylation is complete in about an hour, and the contents of the flask are well washed with hot water, and finally with dilute ammonia. The resinous product is dissolved in hot dilute alcohol and allowed to crystallise, when the dibenzoyl-derivative is obtained in the form of colourless, rhomboidal tablets, melting at 178°.

0.0954 gram gave 5.7 c.c. moist N at 17.5° C. and 754.5 mm. bar.

	Calculated for	Found.
	$C_6H_4 \cdot \begin{matrix} N(C_7H_7) \cdot C_7H_5O \\ NH \cdot C_7H_5O \end{matrix}$	
N .....	6.86	6.86

*Oxidation of a Mixture of Benzylmeta- and Benzylpara-phenylene-diamine.*

Equal molecular proportions of the two diamines in the form of their dihydrochlorides were dissolved in cold water, and the necessary quantity of a solution of potassium dichromate added. A bulky precipitate of a deep indigo-blue colour at once separates. This colouring matter (indamine) was collected, washed well with cold water, in which it is practically insoluble, drained, and dried. The compound when dry forms a blue powder, very similar in appearance to indigo. We have not been able to obtain the substance sufficiently pure to confirm its formula by analysis, as it is insoluble in water, and although soluble in alcohol, does not crystallise from this solvent. There can be but little doubt, however, that the compound is a dibenzyl-amido-indamine:—



The indamine is fairly stable in alcoholic solution, and can be boiled for some time in the presence of this solvent without under-

going decomposition. The solution is of an intense blue colour, which is changed to red both by acids and alkalis. The base thrown out by the addition of an alkali rapidly changes into the azine. Platinic chloride added to the alcoholic solution causes the separation of a deep indigo-blue, amorphous precipitate. A specimen of this platinochloride, collected and washed with alcohol till the washings came through colourless, gave on analysis numbers approximating to the formula  $(C_{26}H_{24}N_4 \cdot HCl)_2PtCl_4$ , but it was not found possible to obtain this salt in a state of perfect purity. The indamine on reduction might be expected to furnish dibenzyltriamidodiphenylamine, but the reduction product passes back into the indamine so rapidly by the action of atmospheric oxygen, that our efforts to isolate this base were unsuccessful. On boiling the indamine suspended in water made slightly acid with hydrochloric acid, the azine is readily formed.

This compound has the formula  $C_7H_7 \cdot NH \cdot C_6H_3 < \begin{smallmatrix} N \\ | \\ N \end{smallmatrix} > C_6H_3 \cdot NH \cdot C_7H_7$ ,

and is a dibenzyl-derivative of diamidophenazine. The hydrochloride and the base are both insoluble in water, and could not be obtained in a crystalline form. The base is slightly soluble in alcohol, the solution being red, with a greenish fluorescence. The hydrochloride is readily soluble in alcohol, the solution being of an intense red, which is changed to violet by excess of hydrochloric acid. On adding platinic chloride solution to the alcoholic solution of the hydrochloride, a reddish-brown, amorphous platinochloride is precipitated. A specimen of this salt, collected and washed repeatedly with alcohol and dried in the water-oven, gave the following results:—

0.0123 gram gave 0.0020 gram Pt = 16.26 per cent.

This agrees with the formula  $(C_{26}H_{22}N_4 \cdot HCl)_2PtCl_4$ , which requires 16.34 per cent. of Pt. A chlorine determination in the platinum salt showed, however, that the compound was still impure, and want of material prevented further attempts at purification.

A specimen of the azine-base was analysed, with the following results:—

0.1671 gram dried for some days under a desiccator in a vacuum over calcium chloride, and then dried in the water-oven till the weight was constant, lost 0.0064 gram = 3.83 per cent.

0.1208 gram (dried in water-oven) gave 13.9 c.c. moist N at 21° and 762.6 mm. bar.

The base dried under a desiccator thus appears to contain 3 mols. of water, one of which is given off at 100°.

Loss calculated for		Found.
$C_{26}H_{22}N_4 \cdot 3H_2O - H_2O.$		
$H_2O$ .....	4.05	3.83
Calculated for		Found.
$C_{26}H_{22}N_4 \cdot 2H_2O.$		
$N$ .....	13.14	13.11

The azine dissolves in strong hydrochloric acid, giving a dull, slate-coloured solution. In strong sulphuric acid it dissolves with an ochreous colour, which first becomes greenish, then violet, and finally red on dilution with water.

#### TETRABENZYLPARAPHENYLENEDIAMINE.

This compound was in the first place obtained in the course of an attempt to prepare a symmetrical dibenzylparaphenylenediamine isomeric with that described by Matzudaira (*Ber.*, 1887, 1614). Paraphenylenediamine sulphate was dissolved in water, the necessary quantity of benzyl chloride (two molecular proportions) added, and the solution made alkaline with caustic soda. The contents of the flask were kept just at the boiling point for about two days, the reaction being promoted by frequent agitation. The product consisted of a semi-solid mass, which was washed with water, and then extracted two or three times with hot alcohol, in which the greater portion remained undissolved. The substance was then crystallised from glacial acetic acid, and finally from benzene and petroleum. The analytical results showed that the substance was the tetrabenzyl-derivative, and subsequent experiments showed that the benzylation always proceeded further than the formation of the dibenzyl-diamine.

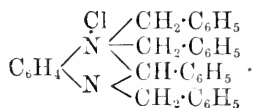
In order to prepare the tetrabenzyl-derivative, it is only necessary to heat paraphenylenediamine or its monobenzyl-derivative with the necessary quantity of benzyl chloride, in the presence of aqueous caustic soda, in the manner above described. When the reaction is complete, the product forms a brittle resin, which can be purified by crystallisation from glacial acetic acid, and then from benzene and petroleum. A specimen thus purified was obtained in the form of a white, crystalline powder, melting at  $149^\circ$ . After another crystallisation, by dissolving in chloroform and throwing out by the addition of alcohol, the melting point remained unaltered.

0.0861 gram gave 0.2735 gram  $CO_2$  and 0.0581 gram  $H_2O$ .

0.1167 gram gave 6 c.c. moist N at  $20^\circ C.$  and 766.1 mm. bar.

	Calculated for $C_6H_4 \begin{smallmatrix} N(C_6H_5)_2 \\ N(C_6H_5)_2 \end{smallmatrix}$	Found.
C .....	87.18	86.64
H .....	6.73	7.46
N ..	5.98	5.92

Tetrabenzylparaphenylenediamine possesses no basic properties. It dissolves with difficulty in boiling alcohol, acetone, or petroleum, separating from these solvents on cooling in the form of slender, white needles, having a silky lustre. The substance dissolves readily in chloroform, benzene, and carbon disulphide; less freely in cold ether. The solution in hot glacial acetic acid deposits the substance on slow cooling, in the form of dense, colourless, prismatic needles. In its behaviour towards oxidising agents the substance closely resembles the corresponding tetramethyl-derivative described by Wurster (*Ber.*, 1886, 3195). The tetrabenzyl-diamine, when dry, does not discolour on exposure to the air, but its solution, in certain solvents, gradually acquires a blue-violet colour. This was first noticed in the case of the acetic acid solution, which becomes deeply coloured on heating, and on continuing to boil the colour gradually disappears. On cooling, the acetic acid solution again becomes slowly coloured. The addition of a chromate to the acid solution causes the immediate separation of an intense blue-violet colouring matter. We have not prepared this colouring matter in sufficient quantity to make an analysis of it, but Wurster states that the corresponding tetramethyl-violet differs from the tetramethyldiamine only by two atoms of hydrogen, and he assigns a formula which, by analogy, would lead to the following formula for the hydrochloride of the tetrabenzyl-violet :—



White filter-paper, wetted with a benzene solution of the tetrabenzyl-diamine and allowed to dry, can be used as a test for "active" oxygen, in the same way as Wurster's tetramethylparaphenylenediamine paper. When sodium nitrite is added to the acetic acid solution of the tetrabenzyl-diamine, the violet colouring matter is first produced, and as the nitrous acid continues to act, the colour gradually changes to orange, and the addition of water then precipitates an orange resinous substance, which is probably a nitrosamine.

## TETRABENZYLMETAPHENYLENEDIAMINE.

This compound was prepared like the preceding, by heating a solution of metaphenylenediamine in the presence of excess of aqueous caustic soda with the calculated quantity of benzyl chloride. In about 12 hours the benzylation was complete, and the product formed a pitchy mass, which was washed repeatedly with water, and then with hot alcohol. The tetrabenzylamine is devoid of all basic properties, and is characterised by general inertness; it is not acted upon by sodium nitrite in acetic acid solution, so that a nitroso-derivative could not be prepared as Witt has shown to be possible in the case of the corresponding tetramethyl-derivative (*Ber.*, 1885, 877). It does not appear to be nitrated even on heating with fuming nitric acid. In its behaviour towards solvents the substance closely resembles the corresponding para-compound, but it is quite uncrystallisable, and separates from its solutions as a resin. A specimen was purified for analysis by dissolving the crude substance in glacial acetic acid, and precipitating by dilution with alcohol. The substance, after being collected and washed with alcohol, formed a light ochreous powder, non-crystalline, and having a melting point of about 80—81°.

0.1328 gram gave 7 c.c. moist N at 18° C. and 755.8 mm. bar.

	Calculated for	
	$C_6H_4 < \begin{matrix} N(C_7H_7)_2 \\ N(C_7H_7)_2 \end{matrix}$	Found.
N .....	5.98	6.00

During the purification of the substance by the above treatment it was noticed that some bye-product, having an intense greenish fluorescence, remained dissolved in the mother-liquor, but this compound has not yet been isolated.

*Finsbury Technical College,*  
*July, 1889.*

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LVIII.—*Contributions to the Chemistry of the Azonaphthols.*

By RAPHAEL MELDOLA, F.R.S., and GILBERT T. MORGAN.

I. ALKYL-DERIVATIVES OF AZO- $\beta$ -NAPHTHOL COMPOUNDS.

IN a recent communication on this subject (this vol., p. 114) it was pointed out that the evidence derived from a study of the products of reduction of the azo- $\beta$ -naphthol-alkoyl-derivatives, indicated that the replaceable atom of hydrogen was attached to oxygen and not to nitrogen; a conclusion which obviously necessitates the rejection of the formulæ proposed for these compounds by Liebermann (*Ber.*, 1883, 2858) and Zincke (*Ber.*, 1884, 3026). Of the alkyl-derivatives of the azo- $\beta$ -naphthol compounds the only one which has been studied in any detail is the ethyl-derivative of benzeneazo- $\beta$ -naphthol (Weinberg, *Ber.*, 1887, 3171). A quantity of this substance having been placed at our disposal by Dr. Weinberg, we thought it of sufficient interest, in connection with the present inquiry, to make a further study of the products of reduction. The substance forwarded to us by Dr. Weinberg consisted of a deep orange-red, viscid oil, which deposited dense, orange crystals on standing for some weeks. The crystals consisted of unaltered benzeneazo- $\beta$ -naphthol, the oily portion consisting of the ethyl-derivative, saturated with the dissolved unalkylated compound. We afterwards prepared other specimens by cohobating benzeneazo- $\beta$ -naphthol dissolved in alcohol with equal molecular proportions of potassium hydroxide and ethyl bromide or iodide. In none of our experiments was the ethylation complete, and we can fully confirm Weinberg's statement that the product always contains a certain quantity of unalkylated substance.

The fact that benzeneazo- $\beta$ -naphthol cannot be alkylated completely, diminishes the value of this and similar compounds for the particular purposes of our present investigation, inasmuch as the products of reduction of the mixture must necessarily contain amido- $\beta$ -naphthol. Sufficient evidence that the ethyl-group is attached to the oxygen-atom has, however, been obtained to warrant the publication of the results. The oily mixture was dissolved in alcohol and reduced by adding a solution containing a little more than the theoretical quantity of stannous chloride. The mixture was allowed to stand at the ordinary temperature for some hours, and the reduction then completed by gently warming, with the addition of some more tin and hydrochloric acid. The alcohol was distilled off, the solution diluted with water, filtered in order to remove resinous impurities, and the

filtrate mixed with dilute sulphuric acid. The sulphate of the naphthylphenyl base slowly separated, and after being collected and washed with cold water, was purified by crystallisation from boiling water. This salt and the free base were found to possess the characters assigned to them by Weinberg, and were not further examined. In order to further characterise the substance, the acetyl-derivative was prepared by boiling the sulphate with glacial acetic acid, dry sodium acetate, and acetic anhydride. The product thrown out by dilution with water was crystallised two or three times from alcohol, and then formed small, flat, whitish needles, melting above  $288^{\circ}$ . Analysis showed the compound to be the diacetyl-derivative of the diamido-naphthylphenylethoxy-compound:—

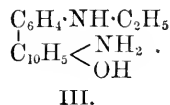
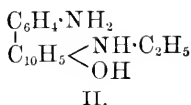
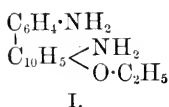
0.0760 gram gave 0.2017 gram  $\text{CO}_2$  and 0.0397 gram  $\text{H}_2\text{O}$ .

0.0812 gram gave 5.4 c.c. moist N at  $11^{\circ}$  C. and 759.6 mm. bar.

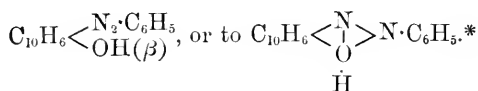
	Calculated for $\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_3$ .	Found.
C.....	72.92	72.66
H.....	6.07	5.80
N.....	7.73	7.92

The filtrate, still containing tin salts, after the removal of the sulphate of the naphthylphenyl-base, was saturated with sulphuretted hydrogen, the tin sulphide filtered off, and the filtrate evaporated to the crystallising point. The white, crystalline deposit was found to consist of amido- $\beta$ -naphthol salts, the base being identified by the usual tests as well as by conversion into the dibenzoyl-derivative (m. p.  $226.5^{\circ}$ , Trans., 1889, 121). This amido- $\beta$ -naphthol is doubtless derived from the unalkylated benzeneazo- $\beta$ -naphthol.

Three formulæ are possible for the naphthylphenyl-base, according to the view taken with respect to the position of the ethyl-group, viz.:—

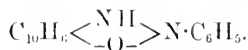


The first of these corresponds to the old formula for benzeneazo- $\beta$ -naphthol:—

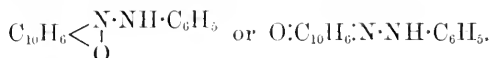


\* Meldola, *Phil. Mag.*, Nov. 1888, 403.

The second formula, which represents the ethyl attached to the nitrogen, would correspond to Liebermann's formula—



The third formula, in which the ethyl is attached to the amidic nitrogen of the phenyl residue, would correspond to Zincke's hydrazone formula:—



The determination of the number of amido-groups in the naphthyl-phenyl base is therefore a matter of considerable importance, as by this means alone is it possible to decide between the different formulæ. Acetylation is obviously of no avail in this case, as a free hydroxyl-group in the ortho-position is acetylated quite as readily as an amido-group (this vol., p. 121). By titration with sodium nitrite, Weinberg has already come to the conclusion that two amido-groups are present, in which case formula I. must be regarded as established. As so much depends upon the decision of this point, we thought it desirable to obtain further evidence, and we accordingly prepared the secondary azo-compound by diazotising the naphthylphenyl-base and combining it with  $\beta$ -naphthol. For this purpose, the hydrochloride of the base was dissolved in water, and treated with a solution containing the calculated quantity of sodium nitrite (two molecular proportions). After standing for some time, the solution was gradually mixed with a well-cooled solution of  $\beta$ -naphthol (two molecular proportions) dissolved in caustic soda. A deep violet precipitate at once formed, and this was collected, washed, and dried. The azo-compound had to be crystallised several times from glacial acetic acid and finally from a mixture of chloroform and alcohol before it was obtained quite pure. The following results were obtained on analysis:—

- I. 0.0839 gram gave 0.2371 gram  $\text{CO}_2$  and 0.0397 gram  $\text{H}_2\text{O}$ .  
 II. 0.0915        „        0.2599        „        „        0.0443        „  
 III. 0.0780        „        6.2 c.c. moist N at  $15^\circ \text{C}$ . and 771.1 mm. bar.

These results agree with the formula of a secondary azo-compound:—

	Calculated for $\text{C}_{38}\text{H}_{28}\text{N}_4\text{O}_3$ .	Found.		
		I.	II.	III.
C .....	77.55	77.07	77.46	—
H .....	4.76	5.25	5.37	—
N .....	9.52	—	—	9.33
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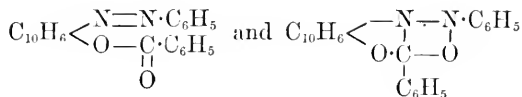
dealing with different compounds. The analyses showed, however, that this was not the case, and we have come to the conclusion that we have here a case of true isomerism or possibly of polymerism. The melting points were found to be—

Prismatic crystals.....	118—119°
Ochreous powder .....	121—121·5°

- I. 0·1349 gram (prismatic form) gave 0·3832 gram CO<sub>2</sub> and 0·0583 gram H<sub>2</sub>O.
- II. 0·1417 gram (ochreous form) gave 0·4052 gram CO<sub>2</sub> and 0·0604 gram H<sub>2</sub>O.
- III. 0·1191 gram (ochreous form) 0·3408 gram CO<sub>2</sub> and 0·0497 gram H<sub>2</sub>O.
- IV. 0·1368 gram (prismatic form) gave 9·3 c.c. moist N at 11·5° C. and 760·3 mm. bar.
- V. 0·1046 gram (ochreous form) gave 7·3 c.c. moist N at 14° C. and 749·4 mm. bar.

	Calculated for C <sub>10</sub> H <sub>6</sub> < $\begin{smallmatrix} \text{N}_2\cdot\text{C}_6\text{H}_5 \\ \text{O}\cdot\text{C}_7\text{H}_5\text{O} \end{smallmatrix}$	Found.				
		I.	II.	III.	IV.	V.
C .....	78·41	77·99	77·99	78·04	—	—
H .....	4·54	4·83	4·72	4·65	—	—
N .....	7·95	—	—	—	8·07	8·09

In addition to their difference in appearance the two forms differ also in other properties. Thus the prismatic form is soluble in boiling alcohol, while the ochreous form is almost insoluble. These differences are certainly suggestive of a difference in constitution, and it is not improbable that we may have an instance of tautomerism (Laar, *Ber.*, 1885, 648) between the forms—



The first of these formulæ would be the most probable for the prismatic form, which resembles a true azo-compound in its general appearance and characters.

Benzeneazo- $\alpha$ -naphthyl benzoate is easily reduced in alcoholic solution by stannous chloride; the product is a basic substance which oxidises rapidly in contact with the air, and we have therefore been unable to isolate it.

## III. NITRATION OF AZONAPHTHOL-DERIVATIVES.

It is well known that both benzeneazo- $\alpha$ -naphthol and benzeneazo- $\beta$ -naphthol are decomposed by nitric acid with the formation of dinitro- $\alpha$ -naphthol and dinitro- $\beta$ -naphthol respectively. In view of this circumstance, it appeared to us likely that additional light would be thrown on the constitution of these azo-compounds by studying the action of nitric acid upon their alkyl- and alkoyl-derivatives.

*Nitration of Benzeneazo- $\beta$ -naphthyl Ethylate.*

The oily ethyl-derivative of benzeneazo- $\beta$ -naphthol dissolves in strong nitric acid (sp. gr. 1.42) in the cold, with the formation of a deep crimson solution. This solution no doubt contains the nitrate of the azo-compound, since Liebermann has already shown that benzeneazo- $\beta$ -naphthol possesses distinctly basic properties (*Ber.*, 1883, 2-60). On allowing the solution to stand for about an hour in the cold, or immediately on warming, the red colour disappears, nitrogen is given off, and the solution on cooling solidifies to a crystalline pulp. The crystalline mass poured on to ice, collected, washed with water, and crystallised two or three times from alcohol, furnished a product consisting of long, straw-coloured needles melting at 135—139°. The melting point was not changed by further crystallisation, and the substance was identified as the ethyl-derivative of dinitro- $\beta$ -naphthol, the melting point of which is generally given as 138° (Graebe and Drew, *Ber.*, 1884, 1172).

0.1176 gram gave 10.8 c.c. moist N at 18° C. and 758 mm. bar.

	Calculated for	Found.
	$C_{10}H_5(NO_2)_2 \cdot O \cdot C_2H_5$ .	
N .....	10.68	10.57

This decomposition of benzeneazo- $\beta$ -naphthyl ethylate by nitric acid furnishes direct proof that the ethyl is attached to the oxygen, and not to the nitrogen-atom.

*Nitration of Benzeneazo- $\alpha$ -naphthyl Ethylate.*

Benzeneazo- $\alpha$ -naphthol was ethylated in alcoholic solution with the theoretical quantities of potassium hydroxide and ethyl iodide. The ethyl-derivative after crystallisation from alcohol formed orange-brown needles melting at 98—100°, as described by Zincke and Bindewald (*Ber.*, 1884, 3028). On adding this ethyl-derivative to cold nitric acid (1.42 sp. gr.), the substance immediately liquefies to

an intensely coloured violet oil. The solution was warmed for a short time in the water-bath, then cooled and poured on to ice, when an ochreous, resinous substance separated. This was collected, washed, and crystallised from dilute alcohol till the melting point was constant. The substance thus obtained consisted of yellowish needles fusing at 91—92°, and was identified as the ethyl-derivative of dinitro- $\alpha$ -naphthol, the melting point of which is generally stated to be 88°.

0.0655 gram gave 6.1 c.c. moist N at 18° C. and 760 mm. bar.

	Calculated for $C_{10}H_5(NO_2)_2 \cdot O \cdot C_2H_5$ .	Found.
N .....	10.68	10.75

The two benzeneazonaphthol ethylates thus decompose in a perfectly analogous manner under the influence of nitric acid.

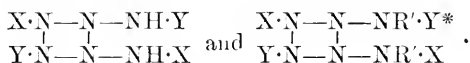
The action of nitric acid upon the derivatives of the azonaphthols containing acid radicles has not been studied in any detail, because the products do not appear to be so definite as those obtained by nitrating the alkyl-derivatives. Benzeneazo- $\alpha$ -naphthyl acetate dissolved in cold nitric acid (sp. gr. 1.42), and allowed to stand for a day, gave on pouring into water, an ochreous resin which, after three crystallisations from glacial acetic acid, furnished a small quantity of a yellowish, crystalline compound melting with decomposition at 163—165°. This substance is the acetyl-derivative of tetranitro- $\alpha$ -naphthol, as it furnishes this last compound (m. p. 180°, Merz and Weith, *Ber.*, 1882, 2715) by hydrolysis. Benzeneazo- $\beta$ -naphthyl acetate dissolves in cold nitric acid with a magenta-red colour which gradually changes into orange, and on pouring the solution into water, an orange precipitate is thrown down which appears to be a nitro-derivative, or a mixture of nitro-derivatives of the azo-compound. The substance has a melting point above 250°, and is so insoluble in most solvents that we have not obtained it sufficiently pure for analysis.

*Finsbury Technical College,  
July, 1889.*

LIX.—*The Synthesis of Heterogeneous Mixed Alkyldiazoamido-compounds.* Preliminary Notice.

By RAPHAEL MELDOLA, F.R.S.

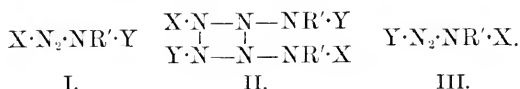
IN a paper recently published by the author and F. W. Streatfeild (this vol., p. 412) it was stated that evidence had been obtained that the mixed diazoamides of the general form  $X \cdot N_3 \cdot H \cdot Y$  had double the molecular weight usually assigned to these compounds. The complete justification of this statement will necessitate a lengthy investigation, and as the work cannot be resumed for some time to come, I propose to give a brief preliminary account of the experimental results thus far obtained. Expressing these results in general terms, it has been found that two isomeric alkyldiazoamides of the forms  $X \cdot N_2 \cdot NR' \cdot Y$  and  $Y \cdot N_2 \cdot NR' \cdot X$ , when boiled together in alcoholic solution in equimolecular proportions, combine with the formation of a product which is identical with that obtained by first preparing the mixed diazoamide  $X \cdot N_3 \cdot H \cdot Y$ , and then alkylating the latter. From this it follows that the mixed diazoamides and their alkyl-derivatives are formed by the coalescence of two single molecules, and their formulæ are accordingly—



It appears from this that the compounds produced by the action of diazotised amines on alkylamines contain the grouping



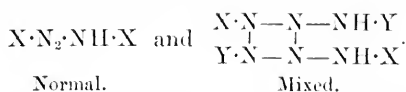
Since the alkyl-derivatives of the normal compounds can also be formed in the same way, *i.e.*, by the action of  $X \cdot N_2 \cdot Cl$  on  $X \cdot NH \cdot R'$ , it follows that the normal compounds also consist of single molecules. The triple isomerism shown to exist in the paper above referred to may therefore be explained by the formulæ—



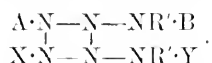
\* These formulæ indicate the existence of "position" isomerides dependent on relative position in the ring of nitrogen-atoms. Evidence has already been obtained that such isomerides are present in the mixed diazo-amides and their alkyl-derivatives, and will be submitted in a later communication.



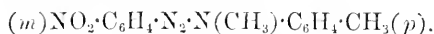
The diazoamides themselves are accordingly referable to the types—



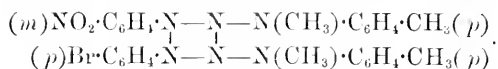
Since the compounds  $X \cdot N_2 \cdot NR' \cdot Y$  and  $Y \cdot N_2 \cdot NR' \cdot X$  combine by simply boiling their solutions together, whilst  $X \cdot N_2 \cdot NR' \cdot X$  and  $Y \cdot N_2 \cdot NR' \cdot Y$  cannot be combined, it seemed a legitimate inference that the grouping  $-N \equiv N - NH-$  or  $-N \equiv N - NR'-$  is stable when the attached radicles are similar and unstable when they are dissimilar, and it appeared highly probable that any pair of alkyl-diazoamides might be combined in a similar manner to the isomeric pairs above formulated. This inference has been completely verified by some preliminary experiments, and the field has thus been opened for the synthesis of what I propose to call heterogeneous mixed diazoamides containing totally different aromatic and fatty radicles. The general formula of such compounds would be—



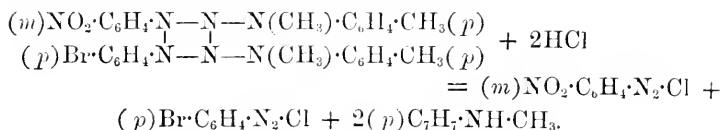
As a type of this class of diazoamides, the following compound has been prepared:—Diazotised metanitriline combined with methylparatoluidine gives the compound



On boiling equimolecular proportions of this and the compound produced by the action of diazotised parabromaniline on methylparabromaniline, a product is obtained which when pure melts at about  $81-82^\circ$ . The formula of this heterogeneous diazoamide is—



The details of the synthesis will be given in a subsequent communication. The compound behaves in every respect like an ordinary mixed diazoamide, being decomposed by cold hydrochloric acid into the usual mixture of diazo-chlorides and alkylamines—



This synthesis and others of a similar character which I have recently effected leave no doubt that the mixed diazoamides have

double the molecular weight usually assigned to them, and the isomerism of the alkyl-derivatives made known in former papers, as well as the other properties of these compounds, is thus, for the first time, rendered intelligible.

*Finsbury Technical College,  
July, 1889.*

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LX.—*Benzophenylhydrazine.*

By S. RUHEMANN, Ph.D., M.A., and F. F. BLACKMAN, B.Sc.

IN a recent number of this Journal (this vol., p. 242) one of us published an investigation on the action of chloroform and alcoholic potash on some hydrazines, and showed how compounds were formed which contain a closed ring of four nitrogen and two carbon-atoms. In turn, that investigation led to the experiments, the results of which form the subject of the present communication.

Doebner (*Annalen*, **210**, 267) acted on phthalanil with benzoyl chloride in the presence of zinc chloride, and obtained phthalylbenzoanilide,  $C_6H_5 \cdot CO \cdot C_6H_4 \cdot N < \begin{smallmatrix} CO \\ CO \end{smallmatrix} > C_6H_4$ , which by alcoholic potash is transformed into amidobenzophenone, or benzoaniline,  $C_6H_5 \cdot CO \cdot C_6H_4 \cdot NH_2$ . This base was regarded by its discoverer as a para-amidobenzophenone, since he was able to transform it into paroxybenzoic acid by converting it into oxybenzophenone, and then fusing the latter with potash. Froehlich (*Ber.*, **17**, 2673), however, showed that a benzophenone-derivative could be obtained from pseudocumidine by a method perfectly analogous to Doebner's. But since the constitution of  $\psi$ -cumidine is expressed by the formula  $C_6H_2 \cdot \overset{1}{CH_3} \cdot \overset{3}{CH_3} \cdot \overset{4}{CH_3} \cdot \overset{6}{NH_2}$ , the benzoyl-group cannot here enter into the para-position, this led him to consider the possibility of benzoaniline being an ortho-compound. In support of this view he adduces the fact that by the action of melted potash molecular transformations take place; and it may be that salicylic acid is the first product of the fusion of the oxybenzophenone from benzoaniline, and that paroxybenzoic acid results from its subsequent transformation. But the experiments of R. Geigy and W. Koenigs (*Ber.*, **18**, 2700) have since proved that Doebner's view of the constitution of benzo-

aniline is correct, and that this base is in reality para-amidobenzophenone.

We have prepared this compound according to Doebner's method, in order to convert it into benzophenylhydrazine, with the object of characterising the latter and applying the isonitrile reaction to it.

*Benzophenylhydrazine.*

The transformation of benzoaniline into the hydrazine was effected by the reduction of the diazo-compound with stannous chloride. For this purpose 20 grams of the paramidobenzophenone were mixed with 400 grams of hydrochloric acid, and the calculated quantity of sodium nitrite (9 grams) dissolved in water, was gradually added to the well-cooled mixture; an interval sufficient for the nitrous smell to disappear being allowed after each addition. When the diazotisation is complete, the solution is filtered and the filtrate poured into a cold solution of 90 grams of stannous chloride in 200 grams of hydrochloric acid. The pale yellow precipitate, which immediately appears, is collected on a linen filter and dried on porous plates; during the drying it gradually becomes orange in colour. To obtain this hydrazine hydrochloride in a state of purity, the orange powder is treated with hot water and the solution filtered, when a considerable quantity of a yellow, insoluble, organic tin-compound is left on the filter. The water used must not be quite at the boiling point, or the hydrazine will be slightly decomposed. When concentrated hydrochloric acid is added to the warm filtrate, faintly coloured needles of the pure hydrazine hydrochloride are deposited, which, after drying in a vacuum, gave on analysis numbers corresponding to the formula  $C_6H_4 \begin{smallmatrix} (1) - CO \cdot C_6H_5 \\ (+) - NH \cdot NH_2 \end{smallmatrix} HCl$  :—

		Found.		
		I.	II.	III.
Calculated for	$C_{13}H_{13}N_2OCl$ .			
N . . . . .	11.27	11.68	11.55	—
Cl. . . . .	14.28	—	—	13.98

The hydrochloride reduces Fehling's solution, dissolves readily in warm water and in alcohol, but is insoluble in hydrochloric acid. The hydrazine sulphate may be prepared by the addition of dilute sulphuric acid to an ethereal solution of the base, when it separates out in white needles, easily soluble in water, but readily decomposed by boiling.

The hydrazine itself can only be prepared satisfactorily by the addition of a concentrated solution of sodium acetate to the slightly

warm solution of the hydrochloride, when it crystallises out in yellow needles. If the acetate be added to the very hot or boiling solution of the hydrochloride, the base is then precipitated in a more or less resinous state. The hydrazine is fairly stable at ordinary temperatures, but at 100° C. it gradually darkens, with slight decomposition. It melts at 127°, is very soluble in alcohol, ether, and benzene, but on evaporating the solutions it is left behind as a resin. The crystals of the hydrazine obtained as above were prepared for analysis by washing with water and drying in a vacuum over sulphuric acid.

The formula  $C_6H_4 \begin{smallmatrix} (1) \\ (4) \end{smallmatrix} \begin{smallmatrix} -CO \cdot C_6H_5 \\ -NH \cdot NH_2 \end{smallmatrix}$ , requires:—

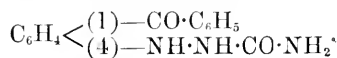
		Found.		
		I. II. III.		
C .....	Theory for $C_{13}H_{12}N_2O$ . 73·58	73·74	—	—
H .....	5·66	5·72	—	—
N .....	13·20	—	13·52	13·23

*Acetylbenzophenylhydrazine*.—Acetic anhydride acts on the hydrazine with evolution of heat. The reaction is completed on the water-bath, the crystalline product purified by treatment with animal charcoal, and recrystallised from hot water. It forms white needles, melting at 154—155°, and easily soluble in alcohol; it gave on analysis values corresponding to the formula  $C_6H_4 \begin{smallmatrix} (1) \\ (4) \end{smallmatrix} \begin{smallmatrix} -CO \cdot C_6H_5 \\ -NH \cdot NH \cdot CO \cdot CH_3 \end{smallmatrix}$ .

		Found.	
		I. II.	
C .....	Theory for $C_{15}H_{14}N_2O_2$ . 70·87	70·72	—
H .....	5·51	5·80	—
N .....	11·02	—	11·14

*Benzophenylsemicarbazide* is formed by adding an aqueous solution of potassium cyanate to a solution of the hydrazine hydrochloride. The resulting precipitate crystallises from boiling water, in which it is difficultly soluble, in slightly coloured crystals, which melt at 215·5° with decomposition and reduce Fehling's solution.

Analysis gave numbers corresponding to the formula



		Found.	
		I. II.	
C .....	Theory for $C_{14}H_{13}N_3O_2$ . 65·88	66·10	—
H .....	5·10	5·37	—
N .....	16·47	—	16·68

*Benzophenyl-phenylsulphosemicarbazide*.—By adding phenyl mustard oil to an ethereal solution of the hydrazine, a sulphosemicarbazide of the formula  $C_6H_4 \begin{smallmatrix} (1) - CO \cdot C_6H_5 \\ (4) - NH \cdot NH \cdot CS \cdot NH \cdot C_6H_5 \end{smallmatrix}$  is obtained. This, after a short time, separates out in yellow crystals difficultly soluble in hot alcohol, from which on cooling they crystallise in plates melting at  $203^\circ$  with decomposition.

They gave on analysis the following results:—

	Calculated for $C_{20}H_{17}N_3OS$ .	Found.	
		I.	II.
N .....	12.10	12.31	—
S .....	9.22	—	9.47

*Benzophenyl-benzaldehyde hydrazine*,  $C_6H_4 \begin{smallmatrix} (1) - CO \cdot C_6H_5 \\ (4) - NH \cdot N : CH \cdot C_6H_5 \end{smallmatrix}$ , is obtained by adding to a warm solution of benzophenylhydrazine hydrochloride a concentrated solution of sodium acetate and benzaldehyde. Alcohol is subsequently added and the solution allowed to stand for some time, when orange crystals separate out; these dissolve with difficulty in hot alcohol, and crystallise from it in yellow glittering plates which melt at  $188^\circ$ . They gave on analysis—

	Theory for $C_{20}H_{15}N_2O$ .	Found.	
		I.	II.
C .....	80.00	80.20	—
H .....	5.33	5.52	—
N .....	9.33	—	9.27

*Benzophenylacetone hydrazine*,  $C_6H_4 \begin{smallmatrix} (1) - CO \cdot C_6H_5 \\ (4) - NH \cdot N : C(CH_3)_2 \end{smallmatrix}$ , is precipitated from a solution of the hydrazine hydrochloride by the addition of acetone and a concentrated solution of sodium acetate. The precipitate is dissolved in hot dilute alcohol, which, on standing, deposits plates melting at  $125^\circ$ , and easily soluble in alcohol and acetone. This substance decomposes after being kept for a few days at ordinary temperatures.

A nitrogen determination of this compound dried in a vacuum gave—

	Calculated for $C_{16}H_{16}N_2O$ .	Found.
N .....	11.11	11.09

*Acetophenone-benzophenylhydrazine*,  $C_6H_4 \begin{smallmatrix} (1) - CO \cdot C_6H_5 \\ (4) - NH \cdot N : C \end{smallmatrix} \begin{smallmatrix} CH_3 \\ C_6H_5 \end{smallmatrix}$ , is prepared in a way quite analogous to that given above for the acetone

compound. It crystallises in bundles of yellow needles which melt at 140—141°. Its composition was confirmed by a nitrogen determination.

	Theory for $C_{21}H_{18}N_2O$ .	Found.
N .....	8.917	9.08

*Benzophenylhydrazine-pyruvic acid*,  $C_6H_5 < \begin{matrix} (1) - CO \cdot C_6H_5 \\ (4) - NH \cdot N : C < \begin{matrix} CH_3 \\ COOH \end{matrix} \end{matrix}$ .

When pyruvic acid is added to a warm aqueous solution of the hydrazine hydrochloride, a lemon-yellow, flocculent precipitate of this substance is at once thrown down. It is soluble in dilute alcohol and crystallises from it in tufts of curved needles which melt at 210° with decomposition.

The following numbers correspond to the formula  $C_{16}H_{14}N_2O_3$  :—

	Theory.	Found.		
		I.	II.	III.
C .....	68.08	68.31	67.75	—
H .....	4.96	5.90	5.19	—
N .....	9.93	—	—	10.14

This acid is easily soluble in alcohol, in alkalis, and ammonia. The barium salt is dissolved by hot water and crystallises from it in yellow needles. The silver salt is thrown down as a yellow precipitate on adding silver nitrate to an ammoniacal solution of the acid. This salt rapidly decomposes and blackens on warming with water.

The *ethyl salt* of this acid is easily formed by heating together on a water-bath, for 1—2 hours, nine parts of absolute alcohol, one part of concentrated sulphuric acid, and one part of the pyruvic acid compound in a flask connected with an inverted condenser. The ethereal salt is then precipitated by the addition of water, washed with dilute ammonia to remove any unaltered pyruvic acid compound, and recrystallised from alcohol. The yellow needles thus obtained melt at 145° without decomposition. On analysis they gave numbers

corresponding to the formula  $C_6H_5 < \begin{matrix} (1) - CO \cdot C_6H_5 \\ (4) - NH \cdot N : C < \begin{matrix} CH_3 \\ COOC_2H_5 \end{matrix} \end{matrix}$ .

	Theory for $C_{18}H_{18}N_2O_3$ .	Found.	
		I.	II.
C .....	69.68	69.73	—
H .....	5.80	6.03	—
N .....	9.03	—	9.29

*Benzoindecarboxylic acid*,  $C_6H_5 \cdot CO \cdot C_6H_3 < \begin{smallmatrix} CH \\ NH \end{smallmatrix} > C \cdot COOH$ , is prepared by heating the finely powdered ethereal salt of benzophenylhydrazine-pyruvic acid with an equal weight of freshly fused zinc chloride at a temperature of  $220^\circ$  in an oil-bath. The mixture melts, darkens, and froths briskly after two or three minutes, at the end of which time the reaction is complete. When cool, the resulting brown mass is powdered and warmed with very dilute hydrochloric acid to remove the zinc chloride. The dark-coloured substance that remains is, with the exception of a little resin, all dissolved by repeated extraction with ether. The ethereal solution is then shaken with dilute soda, from which, on subsequent addition of hydrochloric acid, the indecarboxylic acid is thrown down as a yellow precipitate. To purify this, it is dissolved in ammonia, and the solution boiled with animal charcoal; on addition of hydrochloric acid, it yields a less coloured precipitate which readily dissolves in alcohol and crystallises out in yellowish needles. The acid may be obtained perfectly white, though with a considerable loss of material, by boiling its alcoholic solution with animal charcoal, filtering and concentrating the filtrate. The pure acid melts at  $284\text{--}285^\circ$  with decomposition.

The formula  $C_{16}H_{11}NO_3$  requires—

	Theory.	Found.
C .....	72.45	72.23
H .....	4.15	4.34

This acid is only slightly soluble in boiling water, but dissolves readily in alcohol and in ammonia. The addition of silver nitrate to the latter solution throws down the silver salt as a yellowish, flocculent precipitate. When heated at a temperature between  $280\text{--}290^\circ$ , it gives off carbonic acid and is transformed into *benzoindeole*. The latter was obtained in the form of nearly white needles melting at  $144\text{--}145^\circ$ , by dissolving the melted product in alcohol and decolorising the alcoholic solution by animal charcoal. When dissolved in alcohol, it colours pine shavings moistened with hydrochloric acid, violet, and when acidulated with hydrochloric acid, it is coloured red by potassium nitrite.

We intend to pursue the investigation of this compound.

A small quantity of the ethyl salt of the benzoindecarboxylic acid is contained in the ethereal solution of the product of the zinc chloride condensation, and may be obtained as a yellow residue by evaporating the ether after the free acid has been removed by agitation with sodium hydroxide solution. This residue, dissolved in alcohol, boiled with animal charcoal, and then concentrated, yields

slender needles which melt at 160—161°. The quantity obtained was, however, too small to admit of verification by analysis.

*Action of Chloroform and Alcoholic Potash on Benzophenylhydrazine.*

It was expected that chloroform and alcoholic potash would act on this hydrazine in a manner analogous to that of their action on phenylhydrazine and its homologues, leading to the formation of a tetrazine, as has been shown before (*loc. cit.*) and as will be further seen from a communication shortly to be made to the Society. But the desired compound could not be obtained. When an alcoholic solution of the hydrazine is treated with these agents, it becomes first green and then deep-red in colour. The ethereal extract of the latter, when shaken with dilute sulphuric acid and then evaporated, yields a red resin from which boiling water extracts a small quantity of a crystalline compound, probably formylbenzophenylhydrazine, which is easily decomposed when boiled with water; the same compound appeared also to be formed by heating the hydrazine with formamide at 140° till ammonia ceased to be evolved, but owing to its easy decomposition it could not be recrystallised. All attempts to obtain a crystalline substance from the red resin left after extraction with water entirely failed.

*University Laboratory,  
Cambridge.*

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LXI.—*Further Study of the Thiocarbimides.*

By AUGUSTUS E. DIXON, M.D., Assistant Lecturer in Chemistry,  
Trinity College, University of Dublin.

In a recent communication (Trans., 1880, 300), I described a number of substances obtained by the combination of certain thiocarbimides with primary and secondary amines, and with phenylhydrazine. I hope shortly to describe a further investigation of the hydrazine class of compounds; meanwhile, in the present paper an account will be found—(a) of a number of disubstituted thiocarbamides, hitherto wanting; (b) of the combinations of certain thiocarbimides with piperidine; and (c) of the relations between the thiocarbimides and thialdine.



1. *Methylthiocarbimide and Benzylamine—Methylbenzylthiocarbimide.*

Pure benzylamine, dissolved in alcohol, was added to a warm alcoholic solution containing an equimolecular proportion of methylthiocarbimide. Heat was evolved, and the pungent smell of the thiocarbimide disappeared. After several days' exposure to the air, the mixture assumed the consistence of a thin syrup, from which aggregations of crystalline matter slowly separated. The latter were freed as far as possible from the syrupy mother-liquor by filtration under pressure, and then recrystallised twice from benzene. The substance is very freely soluble in this liquid when hot; but though it is somewhat sparingly so in the cold, the crystallisation is rather tedious, the solution remaining supersaturated for a considerable time. When purified as described, it forms agglomerated masses of dense, white, octahedral crystals, which melt between  $74^{\circ}$  and  $74.5^{\circ}$ .

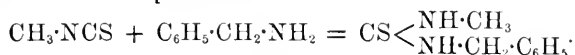
A sulphur determination, made by evaporating the substance to dryness with sodium hydroxide, in a nickel crucible, and fusing the residue with potassium nitrate, afforded 14.41 per cent. of sulphur; theory for  $C_9H_{12}N_2S$  would require 17.79 per cent. This low result was rather unexpected, as the process just indicated gives with suitable compounds very satisfactory results. It was found, however, on further investigation, that this particular compound is difficult of attack by alkalis, even when the latter are concentrated; the loss was therefore due, presumably, to the decomposition at a high temperature of a little unattacked thiocarbimide with evolution of volatile sulphuretted products. This difficulty was easily met by operating as follows:—

0.2034 gram was oxidised with fuming nitric acid on the water-bath; the oxidation-product evaporated to dryness, introduced into a nickel crucible, and again evaporated to dryness with sodium hydroxide. The residue, fused with potassium nitrate, gave 0.2604 gram  $BaSO_4$ ,

Or,  $S = 17.60$  per cent.

Calculated for  $C_9H_{12}N_2S$ ,  $S = 17.79$  „

The action is thus represented:—



Methylbenzylthiocarbimide, when heated with water, melts to somewhat dark-coloured droplets, which just sink in the liquid. These dissolve to a slight extent, and the clear solution, on cooling, becomes milky from the separation of a cloud of minute oily globules, which, after a time, solidify to octahedral crystals. It is extremely

soluble in alcohol; moderately so in ether; its solubility in benzene has already been mentioned.

Ammoniacal silver nitrate, added to either the aqueous or alcoholic solution, gives an immediate black precipitate; but it is curious to note that, just as in the case of the homologous ethylbenzylthiocarbamide (described in the communication before referred to), the solution, either in water or alcohol, is not desulphurised, even by prolonged boiling with alkaline lead tartrate. This resistance to desulphurisation is remarkable, and recalls Lellmann's observation (*Annalen*, **221**, 8; **228**, 248) that boiling with alkaline lead solution fails to remove sulphur from the thiocarbamide-derivatives of the orthodiamines, *e.g.*,  $\text{CS} < \begin{smallmatrix} \text{NH} \\ \text{NH} \end{smallmatrix} > \text{C}_6\text{H}_4$ .

I am inclined to consider that the difficulty in withdrawing the sulphur under the conditions named, is due in some way to the fatty nature of *both* radicles. The data necessary to warrant a general conclusion are, for the most part, only obtainable by direct experiment, but those hitherto obtained seem to point to the view that, in a symmetrical disubstituted thiocarbamide, desulphurisation by lead hydrate is not effected where *both* radicles are of a fatty nature. On the other hand, if either, or both, of the radicles be non-fatty, desulphurisation is easy. Thus, diethylthiocarbamide, in either aqueous or alcoholic solution, is unaffected by boiling with lead hydrate (Hofmann, *Ber.*, **2**, 601). I have also ascertained by direct experiment, that dibenzylthiocarbamide in alcoholic solution is not sensibly desulphurised by boiling with alkaline lead solution. (It is desulphurised instantly, and in the cold, by ammoniacal silver nitrate.) Again, as already recorded (Dixon, *loc. cit.*), ethylbenzylthiocarbamide does not yield its sulphur to alkaline lead tartrate, even at the boiling temperature.

But on the substitution of either or both fatty groups by non-fatty groups, this resistance to desulphurisation seems to be removed. Thus, I have found ethylphenyl-, ethylorthotolyl-, and (*loc. cit.*, 302) benzylphenyl-thiocarbamides all easily desulphurisable; and the same holds good (Hinterberger, *Annalen*, **83**, 346) for ethylallylthiocarbamide. Further, diphenyl-, diorthotolyl-, and (Bizio, *Jahr.*, 1861, 497) allylphenyl-thiocarbamides all readily give up their sulphur, under the conditions named, as does also (Zinin, *Annalen*, **84**, 346) allyl-*x*-naphthylthiocarbamide.

## 2. Methylthiocarbimide and Paratoluidine—Methylparatolylthiocarbamide.

This substance—metameric with the preceding—was obtained by mixing equimolecular proportions of methylthiocarbimide and para-

toluidine, each dissolved in warm, concentrated alcohol. After some time tufts of prismatic crystals began to crystallise out; when nothing further appeared to separate, these were drained off, washed, and recrystallised from boiling alcohol. As thus obtained, the substance forms beautiful vitreous prisms, melting at  $125-126^\circ$  without decomposition.

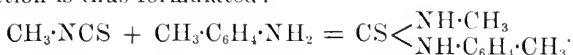
Sulphur was estimated, with the following result:—

0.2070 gram, evaporated to dryness with sodium hydroxide and fused with potassium nitrate, gave 0.2610 gram  $\text{BaSO}_4$ ,

Or,  $\text{S} = 17.81$  per cent.

Calculated for  $\text{C}_9\text{H}_{12}\text{N}_2\text{S}$ ,  $\text{S} = 17.79$  „

The action is thus formulated:—



The yield amounted to nearly 70 per cent. of the theoretical.

Methylparatolylthiocarbamide is slightly soluble in boiling water, almost insoluble in cold. It is moderately soluble in hot alcohol, and freely soluble in ether. Silver nitrate throws down a white precipitate, which soon blackens; the solution is also immediately desulphurised by boiling with alkaline lead tartrate (*cf.* methylbenzylthiocarbamide).

### 3. *Methylthiocarbimide and Orthotoluidine*—*Methylorthotolylthiocarbamide*.

This substance—metameric with the two preceding compounds—was prepared by mixing the theoretic quantities of base and thiocarbimide in concentrated alcoholic solution. No sensible heat was evolved, but after a couple of days the mixture had solidified to a pasty mass; this was recrystallised three times from alcohol, after which the substance separated in pearly-white, flattened, rhombic crystals. The latter melt, without decomposition, between  $152^\circ$  and  $153^\circ$ , that is to say,  $26^\circ$  higher than the corresponding para-compound. When broken up, the dry substance forms a lustrous, flour-like, white powder, which, on friction, becomes strongly electrical, the particles flying about in all directions.

The formula was verified by a sulphur determination:—

0.1808 gram, fused with sodium hydroxide and potassium nitrate, afforded 0.2325 gram  $\text{BaSO}_4$ ,

Or,  $\text{S} = 17.67$  per cent.

Calculated for  $\text{CS} < \begin{matrix} \text{NH}\cdot\text{CH}_3 \\ \text{NH}\cdot\text{C}_7\text{H}_7 \end{matrix}$ ,  $\text{S} = 17.79$  „

The action is formulated as in the preceding case.

The substance is somewhat soluble in boiling water, easily soluble in hot alcohol, moderately in the cold. Ammoniacal silver nitrate added to a cold solution, immediately precipitates silver sulphide, and the solution is also tolerably readily desulphurised by boiling with alkaline lead tartrate.

4. *Allylthiocarbimide and Orthotoluidine*—*Allylorthotolylthiocarbamide*.

Equimolecular proportions of allylthiocarbimide and orthotoluidine were mixed—each in concentrated alcoholic solution. No sensible evolution of heat was observed, but after some days tufts of fine needles began to appear, increasing in quantity until at last the contents of the vessel formed a solid cake. This was removed, pressed, and recrystallised three times from dilute spirit. The recrystallisation is somewhat tedious, the solutions having a tendency to remain supersaturated. Thus purified, the substance forms tufts of small white, prisms, melting between 75° and 76°.

A sulphur determination afforded the following result:—

0.2806 gram, treated with NaOH and KNO<sub>3</sub>, yielded 0.2317 gram BaSO<sub>4</sub>,

Or, S = 15.27 per cent.

Calculated for  $\text{CS} < \begin{smallmatrix} \text{NH} \cdot \text{C}_3\text{H}_5 \\ \text{NH} \cdot \text{C}_7\text{H}_7 \end{smallmatrix}$ , S = 15.54     „

Allylorthotolylthiocarbamide, when heated with water, melts to oily globules, which sink in the liquid. These dissolve to a slight extent, separating again for the most part as the solution cools, in finely-divided droplets, which give the liquid a milky appearance; after a time these droplets solidify to microscopic tufts of pointed prisms. The substance dissolves freely in alcohol and ether, and is soluble also in benzene and in light petroleum. Ammoniacal silver nitrate produces an immediate black precipitate in the cold; the sulphur is also readily removed by warming with alkaline lead solution, with production of a brilliant speculum of galena.

5. *Benzoylthiocarbimide and Orthotoluidine*—*Orthotolylbenzoylthiocarbamide*.

Orthotoluidine was dissolved in alcohol, the vessel cooled by immersion in water, and to the solution a quantity of benzoylthiocarbimide was gradually added in accordance with the equation—



The substances combined vigorously, and tufts of white prisms began at once to separate; in a few minutes the contents of the vessel had set to a solid yellow mass. The latter, on draining and washing with cold alcohol, became almost white. On recrystallisation from boiling alcohol, benzoylorthotolylthiocarbamide was obtained in long, well-formed, transparent prisms possessing a faint yellow tinge, and melting between  $118^{\circ}$  and  $119^{\circ}$ .

Determination of sulphur:—

0.1983 gram, treated with NaOH and  $\text{KNO}_3$ , afforded 0.1775 gram  $\text{BaSO}_4$ ,

Or, S = 12.30 per cent.

Calculated for  $\text{C}_{15}\text{H}_{14}\text{N}_2\text{SO}$ , S = 11.86 „

The substance is insoluble in cold water, moderately soluble in cold alcohol, easily in hot. The solution is blackened immediately on addition of silver nitrate, and is readily desulphurised by boiling with alkaline lead tartrate. Mercuric chloride, added to the alcoholic solution, gives a white, curdy precipitate.

#### 6. Benzoylthiocarbimide and Piperidine—Piperidylbenzoylthiocarbimide.

Gebhardt (*Ber.*, **17**, 3039) has described compounds of piperidine with methyl and some aromatic thiocarbimides. In order to ascertain whether the acid thiocarbimide\* would afford an analogous result, the following experiment was made:—

To 1 mol. prop. piperidine, mixed with anhydrous benzene, was added a benzene solution containing 1 mol. prop. of benzoylthiocarbimide. The substances combined energetically, the heat evolved being sufficient to boil off a portion of the benzene, and the pungent bitter almond-like smell of the thiocarbimide vanished.

The mixture was now exposed freely to the air, in order to allow the residual benzene to evaporate. At the end of a fortnight, there was no sign of crystallisation, the syrupy liquid was therefore placed under the air-pump receiver, where, in a couple of days, it solidified. The solid product, recrystallised twice from spirit, formed fine, silvery-white needles melting at  $122$ — $123^{\circ}$  to a golden-yellow liquid.

Analytical data:—

\* It is curious to note that benzoylthiocarbimide—obtained by Miquel (*Ann. Chim. Phys.* [5], **11**, 300) by the action of benzoyl chloride upon lead thiocyanate—is always referred to as “benzoylthiocyanate.” It is an undoubted thiocarbimide, though differing in some respects (as I hope to show in a future communication) from the alkyl thiocarbimides.

0.2060 gram, burnt with CuO and copper gauze in front, gave 19.6 c.c. nitrogen at 12° and 763 mm.,

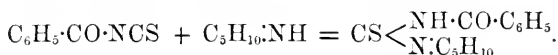
Or, N = 11.34 per cent.

0.2075 gram, treated with NaOH and KNO<sub>3</sub> afforded 0.2040 gram BaSO<sub>4</sub>,

Or, S = 13.51 per cent.

	Calculated for C <sub>13</sub> H <sub>16</sub> N <sub>2</sub> SO.	Experiment.
N .....	11.29	11.34
S .....	12.92	13.51

The following equation represents the action:—

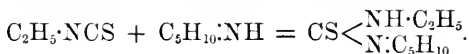


Benzoylpiperidylthiocarbamide is insoluble in water, soluble in alcohol and ether, and freely soluble in benzene. The alcoholic solution gives, with ammoniacal silver nitrate, a white, curdy precipitate, partially soluble on heating. With alcoholic mercuric chloride, a white precipitate is thrown down; and with ferric chloride a deep, reddish-brown colour is produced. The alcoholic solution is *not* desulphurised by boiling with alkaline lead tartrate.

Several attempts were made to obtain from acetylthiocarbimide and piperidine an analogous acetylated piperidylthiocarbamide. The substances combine energetically, but no definite compound could be isolated, though the conditions were varied in several ways. It may be noted here that acetylthiocarbimide, like the corresponding benzoyl-compound, is commonly referred to as a thiocyanate; in fact, Miquel, the discoverer (*loc. cit.*) explicitly denies it admission to the class of thiocarbimides. But, in some cases, it certainly acts as a true "mustard oil;" thus it forms disubstituted thiocarbamides with aniline, the toluidines, and  $\alpha$ -naphthylamine; and, as I recently showed (*Trans.*, 1889, 303), it also behaves as a thiocarbimide towards phenylhydrazine.

#### 7. Ethylthiocarbimide and Piperidine—Ethylpiperidylthiocarbamide.

Alcoholic solutions of ethylthiocarbimide and piperidine were mixed in quantities required by the equation—



Heat was evolved, and the combination was completed by warming on the water-bath until the mixture ceased to smell of the thiocarb-

imide. On evaporation of the alcohol, a brown, oily liquid was left, which, in about 10 days, solidified to a radiating, crystalline mass melting between  $44^{\circ}$  and  $46.5^{\circ}$ . The purification of the substance presented great difficulty; it is extremely soluble in alcohol, ether, acetone, chloroform, amyl alcohol, ethyl acetate, benzene, and carbon bisulphide. It is sparingly soluble in water, from which, however, it separates as an oily liquid which is still impure.

On adding platinic chloride to the alcoholic solution, an orange-brown platinum compound separated as an amorphous powder, which was washed well with spirit, and dried over sulphuric acid. A quantity of this powder was suspended in water through which a current of sulphuretted hydrogen was passed, but this treatment failed to separate the platinum, even when the solution was heated to the boiling point.

The crude substance was now finely ground, washed well with light petroleum, in which it is insoluble, and dried over sulphuric acid for analysis.

0.2084 gram, burnt with CuO and copper gauze in front, gave 28.5 c.c. nitrogen at  $19^{\circ}$  and 767 mm.,

Or, N = 15.97 per cent.

0.1769 gram, treated with  $\text{HNO}_3$ ,\* NaOH, and  $\text{KNO}_3$ , gave 0.2411 gram  $\text{BaSO}_4$ ,

Or, S = 18.73 per cent.

	Calculated for $\text{C}_8\text{H}_{16}\text{N}_2\text{S}$ .	Experiment.
N .....	16.31	15.97
S .....	18.61	18.73

The analytical result is not very satisfactory as regards the nitrogen, but there can be no doubt that the brown, radiating, crystalline mass, referred to above, consists essentially of ethyl-piperidylthiocarbamide.

Ammoniacal silver nitrate produces a yellow precipitate, which blackens slowly on standing, or instantly on heating. Like the preceding compound—benzoylpiperidylthiocarbamide—it is very stable towards alkaline solution of lead, which fails to remove the sulphur even on boiling. This resistance to desulphurisation, I have observed, is also shared by phenylpiperidylthiocarbamide,†

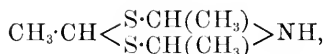
\* *Vide ante*: an estimation in which the treatment with nitric acid was omitted, yielded only 11.9 per cent. of the sulphur.

† This compound was first obtained by Gebhardt (*Ber.*, 17, 3039). A short account of it was subsequently published by Skinner and Ruhemann (*Trans.*, 1888, 558), who appear to have been unaware of Gebhardt's discovery.

which gives up its sulphur to alkaline lead tartrate only on prolonged boiling. The substance dissolves with decomposition in concentrated nitric acid, with production of a dark green colour. Concentrated sulphuric acid also dissolves it on gentle warming; the solution in this case is colourless.

*Thiocarbimides and Thialdine.*

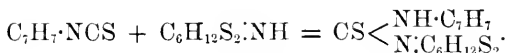
The formula commonly ascribed to thialdine,



assumes it to be an imidic compound, as Gebhardt (*loc. cit.*) has shown that various imidic substances—for example, methylaniline, ethylaniline, piperidine, and conine—can combine with the thiocarbimides to form substituted thiocarbamides, I considered that it would be interesting to ascertain whether, under similar conditions, the complex thialdine residue could be introduced. The results of Marekwald's experiments with thialdine thiocyanate\* rendered it improbable, however, that this would be the case.

*A. Orthotolylthiocarbimide and Thialdine.*

These substances, in alcoholic solution, were mixed in the proportions demanded by the equation—



No sensible rise of temperature occurred, but on slowly evaporating the alcohol, tufts of needles formed in a brown, smeary, evil-smelling liquid. The former, purified by recrystallisation from alcohol, formed thin, white needles melting at 157°. A sulphur determination yielded 12·87 per cent. of S; the compound formulated above (tolylthialdylthiocarbamide) would require 30·7 per cent. The product is, in fact, diorthotolylthiocarbamide:—

	Calculated for $\text{CS}(\text{NH}\cdot\text{C}_7\text{H}_7)_2$ .	Experiment.
S. ....	12·51	12·87

M. p. of  $\text{CS}(\text{NH}\cdot\text{To})_2 = 156$  or  $158^\circ$  (*Ber.*, **4**, 985; **12**, 1854; 2301). Found,  $157^\circ$ .

The experiment was now repeated, using thiocarbanile.

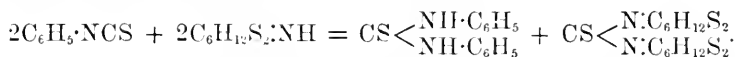
\* Marekwald (*Ber.*, **19**, 1826) found, that on boiling thialdine thiocyanate with water, no thiocarbamide was produced; but the substance decomposed into thioaldehyde,  $\gamma$ -trithioaldehyde, and a compound of the formula  $\text{C}_5\text{H}_9\text{NS}_3$ .



B. *Phenylthiocarbimide and Thialdine.*

Molecular proportions of these substances were mixed under the same conditions as in the previous case. As the alcohol evaporated at the ordinary temperature, leafy crystals separated, the liquid becoming smeary, and at the same time acquiring a penetrating and very disgusting smell. The solid product, recrystallised from alcohol, formed pearly laminae melting at  $152^{\circ}$ . These resembled thiocarbimide (m. p.  $153^{\circ}$ ) in all respects, tasting intensely bitter, and evolving the characteristic odour of thiocarbimide when boiled with concentrated hydrochloric acid. Similar experiments were made, using ethyl- and allyl-thiocarbimides; these afforded results analogous to those already described.

The doubling of the thiocarbimide radicle to form a symmetrical disubstitution-compound is remarkable, and the more so, since the processes were all carried out either at the ordinary temperature of the air, or at a temperature very slightly above it. It would be interesting to ascertain what becomes of the thialdine residue; in all four cases, the bye-product had the same appearance—a somewhat yellowish sticky liquid—and the suggestion naturally offers itself that this might perhaps consist of a dithialdylthiocarbimide, produced according to the equation—



The liquid in question has, however, such a persistent and disgusting smell that I did not care to examine it further.

*Chemical Laboratory,*  
*University of Dublin.*

 LXII.—*Benzylammonium Succinates and their Derivatives.*

By EMIL A. WERNER, F.I.C., Assistant in the Chemical Laboratory of the University of Dublin.

IN the course of a comparative study of the homologues of oxalic acid, to which my work on Chromoxalates (Trans., 1887, **51**, 383, and 1888, **53**, 404) led, I noted incidentally that benzylammonium succinates and their derivatives are practically unknown. Hence, when an opportunity lately presented itself, I prepared a number of these compounds, which are described below:—

1. *Normal Benzylammonium Succinate.*

Di-benzylammonium succinate, prepared by the neutralisation of a cold saturated aqueous solution of succinic acid by pure benzylamine, is soluble in all proportions in water, and by the gradual evaporation of the solution a thick syrup is left, which, on standing over oil of vitriol, ultimately solidifies to a confused semi-crystalline mass. The salt is also freely soluble in strong alcohol, from which it is precipitated by ether as a thick syrup.

However, by very slow evaporation of its alcoholic solution, it was obtained in the form of thin plates, having a greasy lustre, and unctuous to the touch.

A determination of nitrogen in a specimen thus obtained gave the following result:—

0.3335 gram gave 24.1 c.c. of nitrogen at 20° C. and 766 mm. or  
N = 8.29 per cent.

Theory for  $\text{C}_2\text{H}_4 < \begin{smallmatrix} \text{COO} \cdot \text{NH}_3 \cdot \text{C}_7\text{H}_7 \\ \text{COO} \cdot \text{NH}_3 \cdot \text{C}_7\text{H}_7 \end{smallmatrix} = 8.43$  per cent.

The crystals of benzylammonium succinate so formed melt at 144—145°, and at a higher temperature decompose into water, succindibenzylamide and succinbenzylimide.

2. *Benzylammonium Hydrogen Succinate.*

This salt was prepared by the addition of succinic acid (1 mol. prop.) to the aqueous solution of the normal succinate (1 mol. prop.).

It is easily soluble in water, from which it crystallises readily in thick, vitreous, somewhat elastic, rectangular prisms; by slow evaporation of their aqueous solution, the crystals may be easily obtained of a considerable size.

A specimen, after powdering and drying by pressure between folds of bibulous paper, gave the following analytical results:—

0.2354 gram heated at 100—110° to a constant weight lost  
0.0182 gram of  $\text{H}_2\text{O}$  = 7.73 per cent.

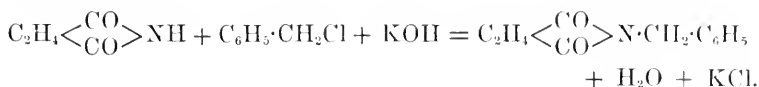
0.2354 gram gave 11.3 c.c. nitrogen at 20° and 772.5 mm., or  
N = 5.55 per cent.

	Found.	Theory for $\text{C}_2\text{H}_4 < \begin{smallmatrix} \text{COO} \cdot \text{NH}_3 \cdot \text{C}_7\text{H}_7 \\ \text{COOH} \end{smallmatrix}, \text{H}_2\text{O}.$
$\text{H}_2\text{O}$ .....	7.73 per cent.	7.40
N.....	5.55 „	5.76

Benzylammonium hydrogen succinate crystallises therefore from water as a monohydrate. The anhydrous salt melts at 116—117°.

3. *Succinbenzylimide*,  $C_2H_4<\overset{CO}{\underset{CO}{>}}N\cdot CH_2\cdot C_6H_5$ .

This compound, which is also produced by the rapid distillation of the benzylammonium succinates, is best prepared by the action of benzyl chloride on a mixture of succinimide and potassium or sodium hydroxide dissolved in strong alcohol. The equation representing its formation is—



On account of secondary actions, resulting in the production of small quantities of benzyl alcohol, benzyl ethyl oxide, and potassium succinamate, the yield of the succinbenzylimide never rises above 60 per cent. of the theoretical.

Succinbenzylimide crystallises from alcohol by spontaneous evaporation in large, brilliant, flat, six-sided prisms, which melt at 98—99°.

The following analytical data were obtained from a specimen twice crystallised from alcohol:—

0.4426 gram gave 28.2 c.c. nitrogen at 16° and 767.5 mm. or  
N = 7.45 per cent.  
0.252 gram burnt with lead chromate gave 0.6446 gram CO<sub>2</sub> and  
0.1356 gram H<sub>2</sub>O.

	Theory for C <sub>11</sub> H <sub>11</sub> NO <sub>2</sub> .	Found.
C.....	69.84 per cent.	69.77
H.....	5.82 „	5.98
N.....	7.40 „	7.45
O.....	16.94 „ (by diff.)	16.80

For the preparation of this compound and isolation of the secondary products, the following method of working gave the best results:—

To 50 grams of succinimide and 28 grams of potassium hydroxide, both dissolved in about 300 c.c. of strong alcohol, 63 grams of benzyl chloride was added, and the mixture digested on the water-bath with reversed condenser, until potassium chloride ceased to separate; for the above quantities, from four to six hours' digestion proved sufficient.\* As the liquid cooled, the new compound separated in beautiful crystals embedded in the potassium chloride: the super-

\* By using a large rounded conical flask, and maintaining the water outside considerably above the level of the liquid within, the boiling may be carried on without interruption.

nant liquid was poured off, and the mixture of chloride and crystals thrown on the filter-pump and washed with alcohol.

From the crystals, the chloride was readily removed by shaking with water. Only one other crop of crystals can generally be obtained by distillation of the mother-liquor, for on concentration the succinbenzylimide ceases to separate in the crystalline form; if the solution be now distilled as far as possible on the water-bath, and the residue shaken up with water, an oil is precipitated and separated; the aqueous solution is shaken up with ether, and the latter is added to the oil; from this ethereal liquid, a third crop of crystals of the succinbenzylimide separates on standing. The aqueous extract of the oil contains any excess of succinimide with a small quantity of potassium succinamate formed during the reaction.

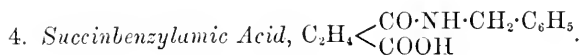
The ethereal solution is then distilled until the temperature reaches about  $220^{\circ}$ . The portion collected between  $170$ — $210^{\circ}$  affords small quantities of benzyl alcohol (b. p.  $204^{\circ}$ ) and benzyl ethyl oxide (b. p.  $185^{\circ}$ ).

The residue in the retort consists of impure succinbenzylimide, which may be obtained either by further distillation or by dissolution in chloroform or benzene, and gradual precipitation of the solution by light petroleum.

Succinbenzylimide is a very stable compound, and distils undecomposed between  $390^{\circ}$  and  $400^{\circ}$ .

It is easily soluble in alcohol, very freely in chloroform and hot benzene, moderately soluble in ether, sparingly soluble in cold carbon bisulphide, more freely in hot, and insoluble in light petroleum; it is moderately soluble in boiling water, from which it is almost completely precipitated on cooling in the form of long, thin, iridescent plates.

When boiled for several hours with alcoholic solutions of caustic potash and soda, it is completely decomposed into benzylamine and succinic acid; it undergoes the same decomposition much more readily by heating with fuming hydrochloric acid in a sealed tube at  $145$ — $150^{\circ}$  for one hour; on the other hand, heating with fuming hydrochloric acid under the ordinary pressure, does not affect the decomposition even after several hours' boiling.



This compound is prepared by boiling the imide (2 mol. props.) with an aqueous solution of 1 mol. prop. of barium hydroxide. The reaction, which consists in an assimilation of a single molecule of water by the imide, is complete after 5—10 minutes' boiling; on

adding dilute hydrochloric acid to the product, the new acid is immediately precipitated in thick white flocks, and after washing on a filter is purified by recrystallisation from alcohol, from which it readily separates in very fine, large, flat, oblique prisms. These melt at  $139^{\circ}$  when pure.

A specimen purified by recrystallisation from alcohol and dried at  $100^{\circ}$  gave the following analytical results:—

0.2478 gram gave 13.8 c.c. of nitrogen at  $13^{\circ}$  and 771 mm.

0.2635 gram gave 0.6145 gram  $\text{CO}_2$  and 0.156 gram  $\text{H}_2\text{O}$ .

	Theory for $\text{C}_{11}\text{H}_{13}\text{NO}_3$	Found.
C .....	63.76 per cent.	63.60
H .....	6.28 „	6.57
N .....	6.76 „	6.64
O .....	23.20 „	23.19 (by diff.)

Succinbenzylamic acid is somewhat soluble in boiling water, almost insoluble in the cold, and slightly soluble in boiling benzene, from which it separates completely on cooling in microscopic needles; it is freely soluble in acetone, almost insoluble in ether and carbon bisulphide.

It is not decomposed by heating with water alone in a sealed tube to  $200^{\circ}$ .

The silver salt is precipitated, on addition of silver nitrate to an aqueous solution of the barium salt; when dried it forms a light, crystalline, micaceous powder, possessing a pearly lustre:—

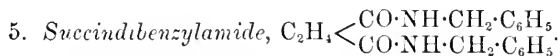
0.292 gram gave on ignition a residue of silver = 0.1001 gram.

	Found.	Theory for $\text{C}_{11}\text{H}_{12}\text{NO}_3\text{Ag}$
Ag .....	34.28 per cent.	34.39

It is insoluble in water or alcohol.

The barium salt crystallises from water in rosette-like aggregates of small prisms, having a pearly lustre. A specimen dried by pressure and air exposure gave:—

Ba = 25.02 per cent. Theory for  $(\text{C}_{11}\text{H}_{12}\text{NO}_3)_2\text{Ba}$  = 24.95 per cent. Ba.



For the preparation of this compound, 10 grams of ethyl succinate were heated in alcoholic solution with 12.5 grams of pure benzylamine for several hours. The diamide separates from its alcoholic solution,

on cooling, in thin crystalline plates, possessing a very brilliant lustre ; these melt at 205—206°. The yield is nearly theoretical.

The following analytical data were afforded by a well-crystallised specimen :—

0·2776 gram gave 23 c.c. of nitrogen at 14° and 756·6 mm.

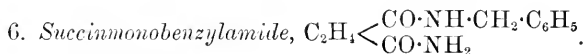
0·2384 gram gave 0·636 gram CO<sub>2</sub> and 0·1520 gram H<sub>2</sub>O.

	Theory for C <sub>15</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub> .	Found.
C .....	72·97 per cent.	72·75
H .....	6·75     ,,	7·08
N .....	9·45     ,,	9·64
O .....	10·83    ,,	10·53 (by diff.).

Succindibenzylamide is sparingly soluble in hot or cold ether, sparingly soluble in chloroform, almost insoluble in carbon bisulphide, slightly soluble in boiling benzene, insoluble in the cold, and insoluble in water.

It is not decomposed by boiling with aqueous soda.

Unsuccessful attempts were made to obtain a mercurial or silver derivative of this diamide ; freshly precipitated mercuric oxide is not acted upon by the boiling alcoholic solution of the amide.



This amide is formed by the action of ammonia on succinbenzylimide, thus :—



For this purpose the succinbenzylimide is heated at 100° for 6—8 hours in a sealed tube with an excess of a strong solution of ammonia in alcohol.

Under these conditions, the yield of the amide never exceeds 30—34 per cent. of theory, and even when the temperature is carried to 200° and maintained for several hours, the yield is not materially increased.

In order to separate the amide, the contents of the tube are evaporated to dryness on the water-bath, and the solid residue is digested with chloroform, which readily dissolves the unaltered imide, leaving behind the amide ; the latter is purified by dissolution in boiling alcohol, from which it separates on cooling in glistening microscopic prisms which melt at 189°.

A specimen, after drying at 100°, gave the following result :—

0.1911 gram gave 22.8 c.c. of nitrogen at 20° and 769 mm.

Theory for		
$C_2H_4 \begin{cases} CO \cdot NH \cdot C_7H_7 \\ CO \cdot NH_2 \end{cases}$		Found.
N . . . . .	13.59 per cent.	13.61 per cent.

Succinmonobenzylamide, in its behaviour towards solvents, resembles the diamide, from which it is readily distinguished by the ease with which it gives off ammonia on boiling with fixed alkali.

On heating, it first melts, and at a higher temperature parts with ammonia, regenerating the imide.

The following comparatively easy decomposition of normal benzylammonium succinate is worthy of note.

A small quantity of the syrupy mother-liquor from some dibenzylammonium succinate was evaporated in a glass dish on the water-bath as far as possible, dried for a couple of hours in a water-oven, and placed in a desiccator over oil of vitriol, where it remained untouched for about seven weeks. On attempting to redissolve the product in water, it was found that a portion representing about 20 per cent. of the whole refused to dissolve. This was collected, washed, and crystallised from hot alcohol, in which it was easily soluble. The crystals which separated were easily seen to be a mixture of two compounds, and the melting point, 196°, did not agree with any compound described in this paper. The crystals were directly digested with chloroform, and a rather sharp separation was thus effected, the products\* so obtained gave the following results:—

I. Product insoluble in chloroform; m. p. 205—206°.

0.1864 gram gave 16 c.c. of nitrogen at 180° C. and 762 mm.

N = 9.88 per cent.

II. Product soluble in chloroform and left as residue on evaporation; m. p. 102—103°.

0.1956 gram gave 13.4 c.c. nitrogen at 17° C. and 760.5 mm., or

N = 7.91 per cent.

Succindibenzylamide.	I. Found.
M. p. 205—206°	M. p. 205—206°.
N . . . . . 9.45 per cent.	9.88 per cent.
Succinbenzylimide.	II. Found.
M. p. 99° C.	M. p. 102—103°.
N . . . . . 7.40 per cent.	7.91 per cent.

\* The quantity of material at my disposal was too small to attempt a further purification.

Considering that the compounds were not quite pure, the analytical results and melting points leave no doubt as to their identity. A few hours' heating in the water-oven and exposure for several weeks over oil of vitriol were, therefore, sufficient to cause a partial loss of the elements of water and benzylamine from anhydrous benzylammonium succinate, and the production of a mixture of the amide and imide.

*University Laboratory,  
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LXIII.—*The Periodic Law of the Chemical Elements.*

By Professor MENDELÉEFF.

(FARADAY LECTURE delivered before the Fellows of the Chemical Society in the Theatre of the Royal Institution, on Tuesday, June 4th, 1889.)

THE high honour bestowed by the Chemical Society in inviting me to pay a tribute to the world-famed name of Faraday by delivering this lecture has induced me to take for its subject the Periodic Law of the Elements—this being a generalisation in chemistry which has of late attracted much attention.

While science is pursuing a steady onward movement, it is convenient from time to time to cast a glance back on the route already traversed, and especially to consider the new conceptions which aim at discovering the general meaning of the stock of facts accumulated from day to day in our laboratories. Owing to the possession of laboratories, modern science now bears a new character, quite unknown not only to antiquity but even to the preceding century. Bacon's and Descartes' idea of submitting the mechanism of science simultaneously to experiment and reasoning has been fully realised in the case of chemistry, it having become not only possible but always customary to experiment. Under the all-penetrating control of experiment, a new theory, even if crude, is quickly strengthened, provided it be founded on a sufficient basis; the asperities are removed, it is amended by degrees, and soon loses the phantom light of a shadowy form or of one founded on mere prejudice; it is able to lead to logical conclusions and to submit to experimental proof. Willingly or not, in science we all must submit not



to what seems to us attractive from one point of view or from another, but to what represents an agreement between theory and experiment; in other words, to demonstrated generalisation and to the approved experiment. Is it long since many refused to accept the generalisations involved in the law of Avogadro and Ampère, so widely extended by Gerhardt? We still may hear the voices of its opponents; they enjoy perfect freedom, but vainly will their voices rise so long as they do not use the language of demonstrated facts. The striking observations with the spectroscope which have permitted us to analyse the chemical constitution of distant worlds, seemed, at first, applicable to the task of determining the nature of the atoms themselves; but the working out of the idea in the laboratory soon demonstrated that the characters of spectra are determined—not directly by the atoms, but by the molecules into which the atoms are packed; and so it became evident that more verified facts must be collected before it will be possible to formulate new generalisations capable of taking their place beside those ordinary ones based upon the conception of simple bodies and atoms. But as the shade of the leaves and roots of living plants, together with the relics of a decayed vegetation, favour the growth of the seedling and serve to promote its luxuriant development, in like manner sound generalisations—together with the relics of those which have proved to be untenable—promote scientific productivity, and ensure the luxuriant growth of science under the influence of rays emanating from the centres of scientific energy. Such centres are scientific associations and societies. Before one of the oldest and most powerful of these I am about to take the liberty of passing in review the 20 years' life of a generalisation which is known under the name of the Periodic Law. It was in March, 1869, that I ventured to lay before the then youthful Russian Chemical Society the ideas upon the same subject, which I had expressed in my just written "Principles of Chemistry."

Without entering into details, I will give the conclusions I then arrived at, in the very words I used:—

"1. The elements, if arranged according to their atomic weights, exhibit an evident *periodicity* of properties.

"2. Elements which are similar as regards their chemical properties have atomic weights which are either of nearly the same value (*e.g.*, platinum, iridium, osmium) or which increase regularly (*e.g.*, potassium, rubidium, caesium).

"3. The arrangement of the elements, or of groups of elements in the order of their atomic weights corresponds to their so-called *valencies* as well as, to some extent, to their distinctive chemical properties—as is apparent among other series in that of lithium, beryllium, barium, carbon, nitrogen, oxygen and iron.

"4. The elements which are the most widely diffused have *small* atomic weights.

"5. The *magnitude* of the atomic weight determines the character of the element just as the magnitude of the molecule determines the character of a compound body.

"6. We must expect the discovery of many yet *unknown* elements, for example, elements analogous to aluminium and silicon, whose atomic weight would be between 65 and 75.

"7. The atomic weight of an element may sometimes be amended by a knowledge of those of the contiguous elements. Thus, the atomic weight of tellurium must lie between 123 and 126, and cannot be 128.

"8. Certain characteristic properties of the elements can be foretold from their atomic weights.

"The aim of this communication will be fully attained if I succeed in drawing the attention of investigators to those relations which exist between the atomic weights of dissimilar elements, which, as far as I know, have hitherto been almost completely neglected. I believe that the solution of some of the most important problems of our science lies in researches of this kind."

To-day, 20 years after the above conclusions were formulated, they may still be considered as expressing the essence of the now well-known periodic law.

Reverting to the epoch terminating with the sixties, it is proper to indicate three series of data without the knowledge of which the periodic law could not have been discovered, and which rendered its appearance natural and intelligible.

In the first place, it was at that time that the numerical value of atomic weights became definitely known. Ten years earlier such knowledge did not exist, as may be gathered from the fact that in 1860 chemists from all parts of the world met at Karlsruhe in order to come to some agreement, if not with respect to views relating to atoms, at any rate as regards their definite representation. Many of those present probably remember how vain were the hopes of coming to an understanding, and how much ground was gained at that Congress by the followers of the unitary theory so brilliantly represented by Cannizzaro. I vividly remember the impression produced by his speeches, which admitted of no compromise, and seemed to advocate truth itself, based on the conceptions of Avogadro, Gerhardt and Regnault, which at that time were far from being generally recognised. And though no understanding could be arrived at, yet the objects of the meeting were attained, for the ideas of Cannizzaro proved, after a few years, to be the only ones which could stand criticism, and which represented an atom as—"the

smallest portion of an element which enters into a molecule of its compound." Only such real atomic weights—not conventional ones—could afford a basis for generalisation. It is sufficient, by way of example, to indicate the following cases in which the relation is seen at once and is perfectly clear:—

K = 39	Rb = 85	Cs = 133
Ca = 40	Sr = 87	Ba = 137

whereas with the equivalents then in use—

K = 39	Rb = 85	Cs = 133
Ca = 20	Sr = 43·5	Ba = 68·5

the consecutiveness of change in atomic weight, which with the true values is so evident, completely disappears.

Secondly, it had become evident during the period 1860–70, and even during the preceding decade, that the relations between the atomic weights of analogous elements were governed by some general and simple laws. Cooke, Cremers, Gladstone, Gmelin, Lenssen, Pettenkofer, and especially Dumas, had already established many facts bearing on that view. Thus Dumas compared the following groups of analogous elements with organic radicles—

Diff.		Diff.		Diff.		Diff.
	Mg = 12		P = 31		O = 8	
Li = 7	Ca = 20	As = 75	S = 16			
Na = 23	Sr = 44	Sb = 119	Se = 40			
K = 39	Ba = 68	Bi = 207	Te = 64			

and pointed out some really striking relationships, such as the following:—

$$F = 19.$$

$$Cl = 35.5 = 19 + 16.5.$$

$$Br = 80 = 19 + 2 \times 16.5 + 28.$$

$$I = 127 = 2 \times 19 + 2 \times 16.5 + 2 \times 28.$$

A. Strecker, in his work "Theorien und Experimente zur Bestimmung der Atomgewichte der Elemente" (Braunschweig, 1859), after summarising the data relating to the subject, and pointing out the remarkable series of equivalents—

Cr = 26.2	Mn = 27.6	Fe = 28	Ni = 29	Co = 30
	Cu = 31.7	Zn = 32.5		

remarks that: "It is hardly probable that all the above-mentioned

relations between the atomic weights (or equivalents) of chemically analogous elements are merely accidental. We must, however, leave to the future the discovery of the *law* of the relations which appears in these figures.”\*

In such attempts at arrangement and in such views are to be recognised the real forerunners of the periodic law; the ground was prepared for it between 1860 and 1870, and that it was not expressed in a determinate form before the end of the decade, may, I suppose, be ascribed to the fact that only analogous elements had been compared. The idea of seeking for a relation between the atomic weights of all the elements was foreign to the ideas then current, so that neither the *vis tellurique* of De Chancourtois, nor the *law of octaves* of Newlands, could secure anybody's attention. And yet both De Chancourtois and Newlands, like Dumas and Strecker, more than Lenssen and Pettenkofer, had made an approach to the periodic law and had discovered its germs. The solution of the problem advanced but slowly, because the facts, and not the law, stood foremost in all attempts; and the law could not awaken a general interest so long as elements, having no apparent connection with each other, were included in the same octave, as for example:—

1st octave of Newlands..	H	F	Cl	Co & Ni	Br	Pd	I	Pt & Ir
7th Ditto....	O	S	Fe	Se	Rh & Ru	Te	Au	Os or Th

Analogies of the above order seemed quite accidental, and the more so as the octave contained occasionally 10 elements instead of eight, and when two such elements as Ba and V, Co and Ni, or Rh and Ru, occupied one place in the octave.† Nevertheless, the fruit was ripening, and I now see clearly that Strecker, De Chancourtois and Newlands stood foremost in the way towards the discovery of the periodic law, and that they merely wanted the boldness necessary to place the whole question at such a height that its reflection on the facts could be clearly seen.

A third circumstance which revealed the periodicity of chemical elements was the accumulation, by the end of the sixties, of new information respecting the rare elements, disclosing their many-sided relations to the other elements and to each other. The

\* “Es ist wohl kaum anzunehmen, dass alle im Vorhergehenden hervorgehobenen Beziehungen zwischen den Atomgewichten (oder Aequivalenten) in chemischen Verhältnissen einander ähnliche Elemente bloss zufällig sind. Die Auffindung der in diesen Zahlen *gesetzlichen* Beziehungen müssen wir jedoch der Zukunft überlassen.”

† To judge from J. A. R. Newlands' work, *On the Discovery of the Periodic Law*, London, 1884, p. 149; “On the Law of Octaves” (from the *Chemical News*, 12, 83, August 15, 1865).

researches of Marignac on niobium, and those of Roscoe on vanadium were of special moment. The striking analogies between vanadium and phosphorus on the one hand, and between vanadium and chromium on the other, which became so apparent in the investigations connected with that element, naturally induced the comparison of  $V = 51$  with  $Cr = 52$ ,  $Nb = 94$  with  $Mo = 96$ , and  $Ta = 192$  with  $W = 194$ ; while, on the other hand,  $P = 31$  could be compared with  $S = 32$ ,  $As = 75$  with  $Se = 79$ , and  $Sb = 120$  with  $Te = 125$ . From such approximations there remained but one step to the discovery of the law of periodicity.

The law of periodicity was thus a direct outcome of the stock of generalisations and established facts which had accumulated by the end of the decade 1860—1870: it is an embodiment of those data in a more or less systematic expression. Where, then, lies the secret of the special importance which has since been attached to the periodic law, and has raised it to the position of a generalisation which has already given to chemistry unexpected aid, and which promises to be far more fruitful in the future and to impress upon several branches of chemical research a peculiar and original stamp? The remaining part of my communication will be an attempt to answer this question.

In the first place we have the circumstance that, as soon as the law, made its appearance, it demanded a revision of many facts which were considered by chemists as fully established by existing experience. I shall return, later on, briefly to this subject, but I wish now to remind you that the periodic law, by insisting on the necessity for a revision of supposed facts, exposed itself at once to destruction in its very origin. Its first requirements, however, have been almost entirely satisfied during the last 20 years; the supposed facts have yielded to the law, thus proving that the law itself was a legitimate induction from the verified facts. But our inductions from data have often to do with such details of a science so rich in facts, that only generalisations which cover a wide range of important phenomena can attract general attention. What were the regions touched on by the periodic law? This is what we shall now consider.

The most important point to notice is, that periodic functions, used for the purpose of expressing changes which are dependent on variations of time and space, have been long known. They are familiar to the mind when we have to deal with motion in closed cycles, or with any kind of deviation from a stable position, such as occurs in pendulum-oscillations. A like periodic function became evident in the case of the elements, depending on the mass of the atom. The primary conception of the masses of bodies or of the masses of atoms belongs to a category which the present state of science forbids us to discuss, because as yet we have no means of dissecting or

analysing the conception. All that was known of functions dependent on masses derived its origin from Galileo and Newton, and indicated that such functions either decrease or increase with the increase of mass, like the attraction of celestial bodies. The numerical expression of the phenomena was always found to be proportional to the mass, and in no case was an increase of mass followed by a recurrence of properties such as is disclosed by the periodic law of the elements. This constituted such a novelty in the study of the phenomena of nature that, although it did not lift the veil which conceals the true conception of mass, it nevertheless indicated that the explanation of that conception must be searched for in the masses of the atoms; the more so, as all masses are nothing but aggregations, or additions, of chemical atoms which would be best described as chemical individuals. Let me remark by the way that though the Latin word "individual" is merely a translation of the Greek word "atom," nevertheless history and custom have drawn so sharp a distinction between the two words, and the present chemical conception of atoms is nearer to that defined by the Latin word than by the Greek, although this latter also has acquired a special meaning which was unknown to the classics. The periodic law has shown that our chemical individuals display a harmonic periodicity of properties, dependent on their masses. Now, natural science has long been accustomed to deal with periodicities observed in nature, to seize them with the vice of mathematical analysis, to submit them to the rasp of experiment. And these instruments of scientific thought would surely, long since, have mastered the problem connected with the chemical elements, were it not for a new feature which was brought to light by the periodic law and which gave a peculiar and original character to the periodic function.

If we mark on an axis of abscissæ a series of lengths proportional to angles, and trace ordinates which are proportional to sines or other trigonometrical functions, we get periodic curves of a harmonic character. So it might seem, at first sight, that with the increase of atomic weights the function of the properties of the elements should also vary in the same harmonious way. But in this case there is no such continuous change as in the curves just referred to, because the periods do not contain the infinite number of points constituting a curve, but a *finite* number only of such points. An example will better illustrate this view. The atomic weights—

$$\begin{array}{cccc} \text{Ag} = 108 & \text{Cd} = 112 & \text{In} = 113 & \text{Sn} = 118 \\ \text{Sb} = 120 & \text{Te} = 125 & \text{I} = 127 & \end{array}$$

steadily increase, and their increase is accompanied by a modification of many properties which constitutes the essence of the periodic law.



in which the variables  $n$  and  $t$  are *whole numbers*. Thus, for oxygen,  $n = 2$ , and  $t = 1$ , whence its atomic weight is  $= 15.94$ ; in the case of chlorine, bromine, and iodine,  $n$  has respective values of 3, 6, and 9, while  $t = 7$ , 6, and 9; in the case of potassium, rubidium, and caesium,  $n = 4$ , 6, and 9, and  $t = 14$ , 18, and 20.

Another attempt was made in 1888 by B. N. Tchitchérin. Its author places the problem of the periodic law in the first rank, but as yet he has investigated the alkaline metals only. Tchitchérin first noticed the simple relations existing between the atomic volumes of all alkaline metals; they can be expressed, according to his views, by the formula

$$A(2 - 0.00535An),$$

where  $A$  is the atomic weight, and  $n$  is equal to 8 for lithium and sodium, to 4 for potassium, to 3 for rubidium, and to 2 for caesium. If  $n$  remained equal to 8, during the increase of  $A$ , then the volume would become zero at  $A = 46\frac{2}{3}$ , and it would reach its maximum at  $A = 23\frac{1}{3}$ . The close approximation of the number  $46\frac{2}{3}$  to the differences between the atomic weights of analogous elements (such as  $\text{Cs} - \text{Rb}$ ,  $\text{I} - \text{Br}$ , and so on); the close correspondence of the number  $23\frac{1}{3}$  to the atomic weight of sodium; the fact of  $n$  being necessarily a whole number, and several other aspects of the question, induce Tchitchérin to believe that they afford a clue to the understanding of the nature of the elements; we must, however, await the full development of his theory before pronouncing judgment on it. What we can at present only be certain of is this: that attempts like the two above named must be repeated and multiplied, because the periodic law has clearly shown that the masses of the atoms increase abruptly, by steps, which are clearly connected in some way with Dalton's law of multiple proportions; and because the periodicity of the elements finds expression in the transition from  $\text{RX}$  to  $\text{RX}_2$ ,  $\text{RX}_3$ ,  $\text{RX}_4$ , and so on till  $\text{RX}_8$ , at which point the energy of the combining forces being exhausted, the series begins anew from  $\text{RX}$  to  $\text{RX}_2$ , and so on.

While connecting by new bonds the theory of the chemical elements with Dalton's theory of multiple proportions, or atomic structure of bodies, the periodic law opened for natural philosophy a new and wide field for speculation. Kant said that there are in the world "two things which never cease to call for the admiration and reverence of man: the moral law within ourselves, and the stellar sky above us." But when we turn our thoughts towards the nature of the elements and the periodic law, we must add a third subject, namely, "the nature of the elementary individuals which we discover everywhere around us." Without them the stellar sky itself is inconceivable; and in the atoms we see at once their peculiar indi-



vidualities, the infinite multiplicity of the individuals, and the submission of their seeming freedom to the general harmony of Nature.

Having thus indicated a new mystery of Nature, which does not yet yield to rational conception, the periodic law, together with the revelations of spectrum analysis, have contributed to again revive an old but remarkably long-lived hope—that of discovering, if not by experiment, at least, by a mental effort, the *primary matter*—which had its genesis in the minds of the Grecian philosophers, and has been transmitted, together with many other ideas of the classic period, to the heirs of their civilisation. Having grown, during the times of the alchemists up to the period when experimental proof was required, the idea has rendered good service; it induced those careful observations and experiments which later on called into being the works of Scheele, Lavoisier, Priestley and Cavendish. It then slumbered awhile, but was soon awakened by the attempts either to confirm or to refute the ideas of Prout as to the multiple proportion relationship of the atomic weights of all the elements. And once again the inductive or experimental method of studying Nature gained a direct advantage from the old Pythagorean idea: because atomic weights were determined with an accuracy formerly unknown. But again the idea could not stand the ordeal of experimental test, yet the prejudice remains and has not been uprooted, even by Stas; nay, it has gained a new vigour, for we see that all which is imperfectly worked out, new and unexplained, from the still scarcely studied rare metals to the hardly perceptible nebulae, have been used to justify it. As soon as spectrum analysis appears as a new and powerful weapon of chemistry, the idea of a primary matter is immediately attached to it. From all sides we see attempts to constitute the imaginary substance *helium*\* the so much longed for primary matter. No attention is paid to the circumstance that the helium line is only seen in the spectrum of the solar protuberances, so that its universality in Nature remains as problematic as the primary matter itself; nor to the fact that the helium line is wanting amongst the Fraunhofer lines of the solar spectrum, and thus does not answer to the brilliant fundamental conception which gives its real force to spectrum analysis.

And finally, no notice is even taken of the indubitable fact that the brilliancies of the spectral lines of the simple bodies vary under different temperatures and pressures; so that all probabilities are in favour of the helium line simply belonging to some long since known element placed under such conditions of temperature, pressure, and gravity as have not yet been realised in our experiments. Again, the idea that the excellent investigations of Lockyer of the spectrum of

\* That is, a body having a wave-length equal to 0.0005875 millimetre.

iron can be interpreted in favour of the compound nature of that element, evidently must have arisen from some misunderstanding. The spectrum of a compound body certainly does not appear as a sum of the spectra of its components; and therefore the observations of Lockyer can be considered precisely as a proof that iron undergoes no other changes at the temperature of the sun but those which it experiences in the voltaic arc—provided the spectrum of iron is preserved. As to the shifting of some of the lines of the spectrum of iron while the other lines maintain their positions, it can be explained, as shown by M. Kleiber (*Journal of the Russian Chemical and Physical Society*, 1885, 147), by the relative motion of the various strata of the sun's atmosphere, and by Zöllner's laws of the relative brilliancies of different lines of the spectrum. Moreover, it ought not to be forgotten that if iron were really proved to consist of two or more unknown elements, we simply should have an increase of the number of our elements—not a reduction, and still less a reduction of all of them to one single primary matter.

Feeling that spectrum analysis will not yield a support to the Pythagorean conception, its modern promoters are so bent upon its being confirmed by the periodic law, that the illustrious Berthelot, in his work *Les origines de l'Alchimie*, 1885, 313, has simply mixed up the fundamental idea of the law of periodicity with the ideas of Prout, the alchemists, and Democritus about primary matter.\* But the periodic law, based as it is on the solid and wholesome ground of experimental research, has been evolved independently of any conception as to the nature of the elements; it does not in the least originate in the idea of an unique matter; and it has no historical connection with that relic of the torments of classical thought, and therefore it affords no more indication of the unity of matter or of the compound character of our elements, than the law of Avogadro, or the law of specific heats, or even the conclusions of spectrum analysis. None of the advocates of an unique matter have ever tried to explain the law from the standpoint of ideas taken from a remote antiquity when it was found convenient to admit the existence of many gods—and of an unique matter.

When we try to explain the origin of the idea of an unique primary matter, we easily trace that in the absence of inductions from experiment it derives its origin from the scientifically philosophical attempt at discovering some kind of unity in the immense diversity of individualities which we see around. In classical times

\* He maintains (on p. 309) that the periodic law requires two new analogous elements, having atomic weights of 48 and 64, occupying positions between sulphur and selenium, although nothing of the kind results from any of the different readings of the law.

such a tendency could only be satisfied by conceptions about the immaterial world. As to the material world, our ancestors were compelled to resort to some hypothesis, and they adopted the idea of unity in the formative material, because they were not able to evolve the conception of any other possible unity in order to connect the multifarious relations of matter. Responding to the same legitimate scientific tendency, natural science has discovered throughout the universe a unity of plan, a unity of forces, and a unity of matter, and the convincing conclusions of modern science compel everyone to admit these kinds of unity. But while we admit unity in many things, we none the less must also explain the individuality and the apparent diversity which we cannot fail to trace everywhere. It has been said of old, "Give a fulcrum, and it will become easy to displace the earth." So also we must say, "Give anything that is individualised, and the apparent diversity will be easily understood." Otherwise, how could unity result in a multitude?

After a long and painstaking research, natural science has discovered the individualities of the chemical elements, and therefore it is now capable not only of analysing, but also of synthesising; it can understand and grasp the general and unity, as well as the individualised and the multitudinous. Unity and the general, like time and space, like force and motion, vary uniformly; the uniform admit of interpolations, revealing every intermediate phase. But the multitudinous, the individualised—like ourselves, like the chemical elements, like the members of a peculiar periodic function of elements, like Dalton's multiple proportions—is characterised in another way: we see in it—side by side with a connecting general principle—leaps, breaks of continuity, points which escape from the analysis of the infinitely small—a complete absence of intermediate links. Chemistry has found an answer to the question as to the causes of multitudes; and while retaining the conception of many elements, all submitted to the discipline of a general law, it offers an escape from the Indian Nirvana—the absorption in the universal, replacing it by the individualised. However, the place for individuality is so limited by the all-grasping, all-powerful universal, that it is merely a fulcrum for the understanding of multitude in unity.

Having touched upon the metaphysical bases of the conception of an unique matter which is supposed to enter into the composition of all bodies, I think it necessary to dwell upon another theory, akin to the above conception,—the theory of the compound character of the elements now admitted by some,—and especially upon one particular circumstance which being related to the periodic law is considered to be an argument in favour of that hypothesis.

Dr. Pelopidas, in 1883, made a communication to the Russian Chemical and Physical Society on the periodicity of the hydrocarbon radicles, pointing out the remarkable parallelism which was to be noticed in the change of properties of hydrocarbon radicles and elements when classed in groups. Professor Carnelley, in 1886, developed a similar parallelism. The idea of M. Pelopidas will be easily understood if we consider the series of hydrocarbon radicles which contain, say, 6 atoms of carbon:—

I	II	III	IV	V	VI	VII	VIII
$C_6H_{13}$	$C_6H_{12}$	$C_6H_{11}$	$C_6H_{10}$	$C_6H_9$	$C_6H_8$	$C_6H_7$	$C_6H_6$

The first of these radicles, like the elements of the Ist group, combines with Cl, OH, and so on, and gives the derivatives of hexyl alcohol,  $C_6H_{13}(OH)$ ; but, in proportion as the number of hydrogen atoms decreases, the capacity of the radicles of combining with, say, the halogens increases.  $C_6H_{12}$  already combines with 2 atoms of chlorine;  $C_6H_{11}$  with 3 atoms, and so on. The last members of the series comprise the radicles of acids; thus  $C_6H_8$ , which belongs to the VIth group, gives, like sulphur, a bibasic acid,  $C_6H_8O_2(OH)_2$ , which is homologous with oxalic acid. The parallelism can be traced still further—because  $C_6H_5$  appears as a monovalent radicle of benzene—and with it begins a new series of aromatic derivatives, so analogous to the derivatives of the fat series. Let me also mention another example from among those which have been given by M. Pelopidas. Starting from the alkaline radicle of monomethylammonium,  $N(CH_3)H_3$ , or  $NCH_6$ , which presents many analogies with the alkaline metals of the Ist group, he arrives, by successively diminishing the number of the atoms of hydrogen, at a seventh group which contains cyanogen, CN, which has long since been compared to the halogens of the VIIth group.

The most important consequence which, in my opinion, can be drawn from the above comparison is, that the periodic law, so apparent in the elements, has a wider application than might appear at first sight: it opens up a new vista of chemical evolutions. But, while admitting the fullest parallelism between the periodicity of the elements and that of the compound radicles, we must not forget that in the periods of the hydrocarbon radicles we have a *decrease* of mass as we pass from the representatives of the first group to the next; while in the periods of the elements the mass *increases* during the progression. It thus becomes evident that we cannot speak of an identity of periodicity in both cases, unless we put aside the ideas of mass and attraction, which are the real corner-stones of the whole of natural science and even enter into those very conceptions of

simple bodies which came to light a full hundred years later than the immortal principles of Newton.\*

From the foregoing, as well as from the failures of so many attempts at finding in experiment and speculation a proof of the compound character of the elements and of the existence of primordial matter, it is evident, in my opinion, that this theory must be classed amongst mere utopias. But utopias can only be combatted by freedom of opinion, by experiment, and by new utopias. In the republic of scientific theories freedom of opinions is guaranteed. It is precisely that freedom which permits me to criticise openly the widely diffused idea as to the unity of matter in the elements. Experiments and attempts at confirming that idea have been so numerous that it really would be instructive to have them all collected together, if only to serve as a warning against the repetition of old failures. And, now, as to new utopias which may be helpful in the struggle against the old ones, I do not think it quite useless to mention a *phantasy* of one of my students who imagined that the weight of bodies does not depend upon their mass, but upon the character of the motion of their atoms. The atoms, according to this new utopian, may all be homogeneous or heterogeneous, we know not which; we know them in motion only, and that motion they maintain with the same persistence as the stellar bodies maintain theirs. The weights of atoms differ only in consequence of their various modes and quantity of motion; the heaviest atoms may be much simpler than the lighter ones; thus an atom of mercury may be simpler than an atom of hydrogen—the manner in which it moves causes it to be heavier. My interlocutor even suggested that the view which attributes the greater complexity to the lighter elements finds confirmation in the fact that the hydrocarbon radicles mentioned by Pelopidas, while becoming lighter as they lose hydrogen, change their properties periodically in the same manner as the elements change theirs according as the atoms grow heavier.

The French proverb, *La critique est facile mais l'art est difficile*, however, may well be reversed in the case of all such ideal views, as it is much easier to formulate than to criticise them. Arising from the virgin soil of newly established facts, the knowledge relating to the elements, to their masses, and to the periodic changes of their properties, has given a motive for the formation of utopian hypotheses, probably because they could not be foreseen by the aid of any of the

\* It is noteworthy that the year in which Lavoisier was born (1743)—the author of the idea of elements and of the indestructibility of matter—is later by exactly one century than the year in which the author of the theory of gravitation and mass was born (1643 N.S.). The affiliation of the ideas of Lavoisier and those of Newton is beyond doubt.

various metaphysical systems, and exist, like the idea of gravitation, as an independent outcome of natural science, requiring the acknowledgement of general laws, when these have been established with the same degree of persistency as is indispensable for the acceptance of a thoroughly established fact. Two centuries have elapsed since the theory of gravitation was enunciated, and although we do not understand its cause, we still must regard gravitation as a fundamental conception of natural philosophy, a conception which has enabled us to perceive much more than the metaphysicians did or could with their seeming omniscience. A hundred years later the conception of the elements arose; it made chemistry what it now is; and yet we have advanced as little in our comprehension of simple bodies since the times of Lavoisier and Dalton as we have in our understanding of gravitation. The periodic law of the elements is only 20 years old: it is not surprising therefore that, knowing nothing about the causes of gravitation and mass, or about the nature of the elements, we do not comprehend the *rationale* of the periodic law. It is only by collecting established laws, that is by working at the acquirement of truth, that we can hope gradually to lift the veil which conceals from us the causes of the mysteries of Nature and to discover their mutual dependency. Like the telescope and the microscope, laws founded on the basis of experiment are the instruments and means of enlarging our mental horizon.

In the remaining part of my communication I shall endeavour to show, and as briefly as possible, in how far the periodic law contributes to enlarge our range of vision. Before the promulgation of this law the chemical elements were mere fragmentary, incidental facts in Nature; there was no special reason to expect the discovery of new elements, and the new ones which were discovered from time to time appeared to be possessed of quite novel properties. The law of periodicity first enabled us to perceive undiscovered elements at a distance which formerly was inaccessible to chemical vision; and long ere they were discovered new elements appeared before our eyes possessed of a number of well-defined properties. We now know three cases of elements whose existence and properties were foreseen by the instrumentality of the periodic law. I need but mention the brilliant discovery of *gallium*, which proved to correspond to eka-aluminium of the periodic law, by Lecoq de Boisbaudran; of *scandium*, corresponding to eka-boron, by Nilson; and of *germanium*, which proved to correspond in all respects to eka-silicium, by Winckler. When, in 1871, I described to the Russian Chemical Society the properties, clearly defined by the periodic law, which such elements ought to possess, I never hoped that I should live to mention their discovery to the Chemical Society of Great Britain as

a confirmation of the exactitude and the generality of the periodic law. Now, that I have had the happiness of doing so, I unhesitatingly say that although greatly enlarging our vision, even now the periodic law needs further improvements in order that it may become a trustworthy instrument in further discoveries.\*

I will venture to allude to some other matters which chemistry has discerned by means of its new instrument, and which it could not have made out without a knowledge of the law of periodicity, and I will confine myself to simple bodies and to oxides.

Before the periodic law was formulated the atomic weights of the elements were purely empirical numbers, so that the magnitude of the equivalent, and the atomicity or the value in substitution possessed by an atom, could only be tested by critically examining the methods of determination, but never directly by considering the numerical values themselves; in short, we were compelled to move in the dark, to submit to the facts, instead of being masters of them. I need not recount the methods which permitted the periodic law at last to master the facts relating to atomic weights, and I would merely call to mind that it compelled us to modify the valencies of *indium* and *cerium*, and to assign to their compounds a different molecular composition. Determinations of the specific heats of these two metals fully confirmed the change. The trivalency of *yttrium*, which makes us now represent its oxide as  $Y_2O_3$  instead of as  $YO$ , was also foreseen (in 1870) by the periodic law, and it now has become so probable that Cleve, and all other subsequent investigators of the rare metals, have not only adopted it but have also applied it without any new demonstration to bodies so imperfectly known as those of the cerite and gadolinite group, especially since Hildebrand determined the specific heats of lanthanum and didymium and confirmed the expectations suggested by the periodic law. But here, especially in the case of didymium, we meet with a series of difficulties long since foreseen through the periodic law, but only now becoming

\* I foresee some more new elements, but not with the same certitude as before. I shall give one example, and yet I do not see it quite distinctly. In the series which contains  $Hg = 204$ ,  $Pb = 206$ , and  $Bi = 208$ , we can guess the existence (at the place VI—11) of an element analogous to tellurium, which we can describe as dvi-tellurium, Dt having an atomic weight of 212, and the property of forming the oxide  $DtO_3$ . If this element really exists, it ought in the free state to be an easily fusible, crystalline, non-volatile metal of a grey colour, having a density of about 9.3, capable of giving a dioxide,  $DtO_2$ , equally endowed with feeble acid and basic properties. This dioxide must give on active oxidation an unstable higher oxide,  $DtO_3$ , which should resemble in its properties  $PbO_2$  and  $Bi_2O_5$ . Dvi-tellurium hydride, if it be found to exist, will be a less stable compound than even  $H_2Te$ . The compounds of dvi-tellurium will be easily reduced, and it will form characteristic definite alloys with other metals.

evident, and chiefly arising from the relative rarity and insufficient knowledge of the elements which usually accompany didymium.

Passing to the results obtained in the case of the rare elements *beryllium*, *scandium* and *thorium*, it is found that these have many points of contact with periodic law. Although Avdéeff long since proposed the magnesia formula to represent beryllium oxide, yet there was so much to be said in favour of the alumina formula, on account of the specific heat of the metals and the isomorphism of the two oxides, that it became generally adopted and seemed to be well established. The periodic law, however, as Brauner repeatedly insisted (*Berichte*, 1878, 872; 1881, 53) was against the formula  $\text{Be}_2\text{O}_3$ ; it required the magnesium formula  $\text{BeO}$ , that is, an atomic weight of 9, because there was no place in the system for an element like beryllium having an atomic weight of 13.5. This divergence of opinion lasted for years, and I often heard that the question as to the atomic weight of beryllium threatened to disturb the generality of the periodic law, or, at any rate, to require some important modifications of it. Many forces were operating in the controversy regarding beryllium, evidently because a much more important question was at issue than merely that involved in the discussion of the atomic weight of a relatively rare element; and during the controversy the periodic law became better understood, and the mutual relations of the elements became more apparent than ever before. It is most remarkable that the victory of the periodic law was won by the researches of the very observers who previously had discovered a number of facts in support of the trivalency of beryllium. Applying the higher law of Avogadro, Nilson and Petterson have finally shown that the density of the vapour of the beryllium chloride,  $\text{BeCl}_2$ , obliges us to regard beryllium as bivalent in conformity with the periodic law.\* I consider the confirmation of Avdéeff's and Brauner's view as important in the

\* Let me mention another proof of the bivalency of beryllium which may have passed unnoticed, as it was published in the Russian chemical literature. Having remarked (in 1884) that the density of such solutions of chlorides of metals,  $\text{MCl}_n$ , as contain 200 mols. of water (or a large and constant amount of water) regularly increases as the molecular weight of the dissolved salt increases, I proposed to one of our young chemists, M. Burdakoff, that he should investigate the beryllium chloride. If its molecule be  $\text{BeCl}_2$  its weight must be = 80; and in such a case it must be heavier than the molecule of  $\text{KCl}$  = 74.5, and lighter than that of  $\text{MgCl}$  = 93. On the contrary, if beryllium chloride is a trichloride,  $\text{BeCl}_3$  = 120, its molecule must be heavier than that of  $\text{CaCl}_2$  = 111, and lighter than that of  $\text{MnCl}_2$  = 126. Experiment has shown the correctness of the former formula, the solution  $\text{BeCl}_2 + 200\text{H}_2\text{O}$  having (at  $15^\circ/4^\circ$ ) a density of 1.0138, this being a higher density than that of the solution  $\text{KCl} + 200\text{H}_2\text{O}$  (= 1.0121), and lower than that of  $\text{MgCl}_2 + 200\text{H}_2\text{O}$  (= 1.0203). The bivalency of beryllium was thus confirmed in the case both of the dissolved and the vaporised chloride.



history of the periodic law as the discovery of scandium, which, in Nilson's hands, confirmed the existence of the eka-boron.

The circumstance that *thorium* proved to be quadrivalent, and  $\text{Th} = 232$ , in accordance with the views of Chydenius and the requirements of the periodic law, passed almost unnoticed, and was accepted without opposition, and yet both thorium and uranium are of great importance in the periodic system, as they are its last members, and have the highest atomic weights of all the highest elements.

The alteration of the atomic weight of *uranium* from  $\text{U} = 120$  into  $\text{U} = 240$  attracted more attention, the change having been made on account of the periodic law, and for no other reason. Now that Roscoe, Rammelsberg, Zimmermann, and several others have admitted the various claims of the periodic law in the case of uranium, its high atomic weight is received without objection, and it endows that element with a special interest.

While thus demonstrating the necessity of modifying the atomic weights of several insufficiently known elements, the periodic law enabled us also to detect errors in the determination of the atomic weights of several elements whose valencies and true position among other elements were already well known. Three such cases are especially noteworthy: those of tellurium, titanium and platinum. Berzelius had determined the atomic weight of *tellurium* to be 128, while the periodic law claimed for it an atomic weight below that of iodine, which had been fixed by Stas at 126.5, and which was certainly not higher than 127. Brauner then undertook the investigation, and he has shown that the true atomic weight of tellurium is lower than that of iodine, being near to 125. For *titanium* the extensive researches of Thorpe have confirmed the atomic weight of  $\text{Ti} = 48$ , indicated by the law, and already foreseen by Rose, but contradicted by the analyses of Pierre and several other chemists. An equally brilliant confirmation of the expectations based on the periodic law has been given in the case of the series osmium, iridium, platinum, and gold. At the time of the promulgation of the periodic law the determinations of Berzelius, Rose, and many others gave the following figures:—

$\text{Os} = 200$ ;  $\text{Ir} = 197$ ;  $\text{Pt} = 198$ ;  $\text{Au} = 196$ .

The expectations of the periodic law\* have been confirmed, first, by new determinations of the atomic weight of *platinum* (by Seubert, Dittmar and M'Arthur), which proved to be near to 196 (taking  $\text{O} = 16$ , as proposed by Marignac, Brauner, and others); secondly,

\* I pointed them out in the *Liebig's Annalen*, Supplement Band viii, 1871, p. 211.

by Seubert having proved that the atomic weight of *osmium* is really lower than that of platinum, and that it is near to 191; and thirdly, by the investigations of Krüss, and Thorpe and Laurie proving that the atomic weight of *gold* exceeds that of platinum, and approximates to 197. The atomic weights which were thus found to require correction were precisely those which the periodic law had indicated as affected with errors; and it has been proved therefore that the periodic law affords a means of testing experimental results. If we succeed in discovering the exact character of the periodical relationships between the increments in atomic weights of allied elements discussed by Ridberg in 1885, and again by Bazaroff in 1887, we may expect that our instrument will give us the means of still more closely controlling the experimental data relating to atomic weights.

Let me next call to mind that, while disclosing the variation of chemical properties,\* the periodic law has also enabled us to systematically discuss many of the physical properties of elementary bodies, and to show that these properties are also subject to the law of periodicity. At the Moscow Congress of Russian Naturalists in August, 1869, I dwelt upon the relations which existed between density and the atomic weight of the elements. The following year Professor Lothar Meyer, in his well-known paper,† studied the same subject in more detail, and thus contributed to spread information about the periodic law. Later on, Carnelley, Laurie, L. Meyer, Roberts-Austen, and several others applied the periodic system to represent the order in the changes of the magnetic properties of the elements, their melting points, the heats of formation of their haloid compounds, and even of such mechanical properties as the coefficient of elasticity, the breaking stress, &c., &c. These deductions, which have received further support in the discovery of new elements endowed not only with chemical but even with physical properties which were foreseen by the law of periodicity, are well known; so I need not dwell upon the subject, and may pass to the consideration of oxides.‡

\* Thus, in the typical small period of

Li, Be, B, C, N, O, F,

we see at once the progression from the alkaline metals to the acid non-metals, such as are the halogens.

† *Liebig's Annalen*, Erz. Bd. vii, 1870.

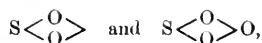
‡ A distinct periodicity can also be discovered in the spectra of the elements. Thus the researches of Hartley, Ciamician, and others have disclosed, first, the homology of the spectra of analogous elements; secondly, that the alkaline metals have simpler spectra than the metals of the following groups; and thirdly, that there is a certain likeness between the complicated spectra of manganese and iron on the one hand, and the no less complicated spectra of chlorine and bromine on

In indicating that the gradual increase of the power of elements of combining with oxygen is accompanied by a corresponding decrease in their power of combining with hydrogen, the periodic law has shown that there is a limit of oxidation, just as there is a well-known limit to the capacity of elements for combining with hydrogen. A single atom of an element combines with at most four atoms of either hydrogen or oxygen: and while  $\text{CH}_4$  and  $\text{SiH}_4$  represent the highest hydrides, so  $\text{RuO}_4$  and  $\text{OsO}_4$  are the highest oxides. We are thus led to recognise types of oxides, just as we have had to recognise types of hydrides.\*

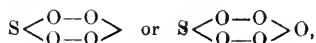
The periodic law has demonstrated that the maximum extent to which different non-metals enter into combination with oxygen is determined by the extent to which they combine with hydrogen, and that the sum of the number of equivalents of both must be equal to 8. Thus chlorine, which combines with 1 atom, or 1 equivalent of hydrogen, cannot fix more than 7 equivalents of oxygen, giving  $\text{Cl}_2\text{O}_7$ ; while sulphur, which fixes 2 equivalents of hydrogen, cannot combine with more than 6 equivalents or 3 atoms of oxygen. It thus becomes evident that we cannot recognise as a fundamental property of the elements the atomic valencies deduced from their hydrides; and that we must modify, to a certain extent, the theory of atomicity if we desire to raise it to the dignity of a general principle capable of affording an insight into the constitution of all compound molecules. In other words, it is only to carbon, which is quadrivalent with regard both to oxygen and hydrogen, that we can apply the theory of constant valency and of bond, by means of which so many still endeavour to explain the structure of compound molecules. But I should go too far if I ventured to explain in detail the conclusions which can be drawn from the above considerations. Still, I think it necessary to dwell upon one particular fact which must be explained from the point of view of the periodic law in order to clear the way to its extension in that particular direction.

the other hand, and their likeness corresponds to the degree of analogy between those elements which is indicated by the periodic law.

\* Formerly it was supposed that, being a bivalent element, oxygen can enter into any grouping of the atoms, and there was no limit foreseen as to extent to which it could further enter into combination. We could not explain why bivalent sulphur, which forms compounds such as



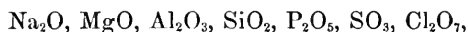
could not also form oxides such as—



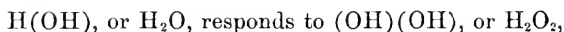
while other elements, as, for instance, chlorine, form compounds such as—



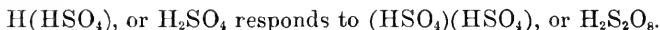
The higher oxides yielding salts the formation of which was foreseen by the periodic system—for instance, in the short series beginning with sodium—



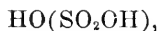
must be clearly distinguished from the higher degrees of oxidation which correspond to hydrogen peroxide and bear the true character of peroxides. Peroxides such as  $\text{Na}_2\text{O}_2$ ,  $\text{BaO}_2$ , and the like have long been known. Similar peroxides have also recently become known in the case of chromium, sulphur, titanium, and many other elements, and I have sometimes heard it said that discoveries of this kind weaken the conclusions of the periodic law in so far as it concerns the oxides. I do not think so in the least, and I may remark, in the first place, that all these peroxides are endowed with certain properties—obviously common to all of them, which distinguish them from the actual, higher, salt-forming oxides, especially their easy decomposition by means of simple contact agencies; their incapacity of forming salts of the common type; and their capacity of combining with other peroxides (like the faculty which hydrogen peroxide possesses of combining with barium peroxide, discovered by Schoene). Again, we remark that some groups are especially characterised by their capacity of generating peroxides. Such is, for instance, the case in the VIth group, where we find the well-known peroxides of sulphur, chromium, and uranium; so that further investigation of peroxides will probably establish a new periodic function, foreshadowing that molybdenum and wolfram will assume peroxide forms with comparative readiness. To appreciate the constitution of such peroxides, it is enough to notice that the peroxide form of sulphur (so-called persulphuric acid) stands in the same relation to sulphuric acid as hydrogen peroxide stands to water:—



and so also—



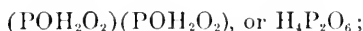
Similar relations are seen everywhere, and they correspond to the principle of substitutions which I long since endeavoured to represent as one of the chemical generalisations called into life by the periodic law. So also sulphuric acid, if considered with reference to hydroxyl, and represented as follows—



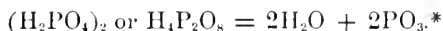
has its corresponding compound in dithionic acid—



Therefore, also, phosphoric acid,  $\text{HO}(\text{POH}_2\text{O}_2)$ , has, in the same sense, its corresponding compound in the subphosphoric acid of Saltzer:—



and we must suppose that the peroxide compound corresponding to phosphoric acid, if it be discovered, will have the following structure:—



As far as is known at present, the highest form of peroxides is met with in the peroxide of uranium,  $\text{UO}_6$ , prepared by Fairley;† while  $\text{OsO}_4$  is the highest oxide giving salts. The line of argument which is inspired by the periodic law, so far from being weakened by the discovery of peroxides, is thus actually strengthened, and we must hope that a further exploration of the region under consideration will confirm the applicability to chemistry generally of the principles deduced from the periodic law.

Permit me now to conclude my rapid sketch of the oxygen compounds by the observation that the periodic law is especially brought into evidence in the case of the oxides which constitute the immense majority of bodies at our disposal on the surface of the earth.

The oxides are evidently subject to the law, both as regards their chemical and their physical properties, especially if we take into account the cases of polymerism which are so obvious when comparing  $\text{CO}_2$  with  $\text{Si}_n\text{O}_{2n}$ . In order to prove this I give the densities  $s$  and the specific volumes  $v$  of the higher oxides of two short periods. To render comparison easier, the oxides are all represented as of the form  $\text{R}_2\text{O}_n$ . In the column headed  $\Delta$  the differences are given between the volume of the oxygen compound and that of the parent element, divided by  $n$ , that is, by the number of atoms of oxygen in the compound:—‡

\* In this sense, oxalic acid,  $(\text{COOH})_2$ , also corresponds to carbonic acid,  $\text{OII}(\text{COOH})$ , in the same way that dithionic acid corresponds to sulphuric acid, and subphosphoric acid to phosphoric; therefore, if a peroxide, corresponding to carbonic acid, be obtained, it will have the structure of  $(\text{HC'O}_3)_2$ , or  $\text{H}_2\text{C}_2\text{O}_6 = \text{H}_2\text{O} + \text{C}_2\text{O}_5$ . So also lead must have a real peroxide,  $\text{Pb}_2\text{O}_5$ .

† The compounds of uranium prepared by Fairley seem to me especially instructive in understanding the peroxides. By the action of hydrogen peroxide on uranium oxide,  $\text{UO}_3$ , a peroxide of uranium,  $\text{UO}_4\cdot 4\text{H}_2\text{O}$ , is obtained ( $\text{U} = 240$ ) if the solution be acid; but if hydrogen peroxide act on uranium oxide in the presence of caustic soda, a crystalline deposit is obtained, which has the composition  $\text{Na}_4\text{UO}_5\cdot 4\text{H}_2\text{O}$ , and evidently is a combination of sodium peroxide,  $\text{Na}_2\text{O}_2$ , with uranium peroxide,  $\text{UO}_4$ . It is possible that the former peroxide,  $\text{UO}_4\cdot 4\text{H}_2\text{O}$ , contains the elements of hydrogen peroxide and uranium peroxide,  $\text{U}_2\text{O}_7$ , or even  $\text{U}(\text{OH})_6\text{H}_2\text{O}_2$ , like the peroxide of tin recently discovered by Spring, which has the constitution  $\text{Sn}_2\text{O}_5\text{H}_2\text{O}_2$ .

‡  $\Delta$  thus represents the average increase of volume for each atom of oxygen con-

	<i>s.</i>	<i>v.</i>	$\Delta$ .		<i>s.</i>	<i>v.</i>	$\Delta$ .
Na <sub>2</sub> O .....	2·6	24	-22	K <sub>2</sub> O .....	2·7	35	-55
Mg <sub>2</sub> O <sub>2</sub> .....	3·6	22	-3	Ca <sub>2</sub> O .....	3·15	36	-7
Al <sub>2</sub> O <sub>3</sub> .....	4·0	26	+1·3	Sc <sub>2</sub> O <sub>3</sub> .....	3·86	35	0
Si <sub>2</sub> O <sub>4</sub> .....	2·65	45	5·2	Li <sub>2</sub> O <sub>4</sub> .....	4·2	38	+5
P <sub>2</sub> O <sub>5</sub> .....	2·39	59	6·2	V <sub>2</sub> O <sub>5</sub> .....	3·49	52	6·7
S <sub>2</sub> O <sub>6</sub> .....	1·96	82	8·7	Cr <sub>2</sub> O <sub>6</sub> .....	2·74	73	9·5

I have nothing to add to these figures, except that like relations appear in other periods as well. The above relations were precisely those which made it possible for me to be certain that the relative density of eka-silicon oxide would be about 4·7; germanium oxide, actually obtained by Winckler, proved, in fact, to have the relative density 4·703.

The foregoing account is far from being an exhaustive one of all that has already been discovered by means of the periodic law telescope in the boundless realms of chemical evolution. Still less is it an exhaustive account of all that may yet be seen, but I trust that the little which I have said will account for the philosophical interest attached in chemistry to this law. Although but a recent scientific generalisation, it has already stood the test of laboratory verification and appears as an instrument of thought which has not yet been compelled to undergo modification; but it needs not only new applications, but also improvements, further development, and plenty of fresh energy. All this will surely come, seeing that such an assembly of men of science as the Chemical Society of Great Britain has expressed the desire to have the history of the periodic law described in a lecture dedicated to the glorious name of Faraday.

#### LXIV.—*The Dissociation of Amine Vapours.*

By G. J. BURCH, B.A. and J. E. MARSH, B.A., University Laboratory, Oxford.

THE theory of Van t' Hoff that there is a definite relationship to space of the four bonds or affinities of the carbon-atom has received such remarkable confirmation from facts, that chemists have very naturally attempted to extend the conception to other elements, especially

tained in the higher salt-forming oxide. The acid oxides give, as a rule, a higher value of  $\Delta$ , while in the case of the strongly alkaline oxides its value is usually negative.

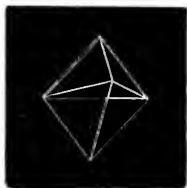
those which enter into the composition of the so-called organic substances.

In making this extension, we are bound to keep in mind the principles of the original conception, namely, that the four valencies of the carbon-atom are directed to the four angles of a tetrahedron of which the atom occupies the centre. In this hypothesis, as we understand it, the equality of the valencies, *inter se*, is represented by the symmetry of direction and the equal length of the vectors from the centre to the four angles. The consistent development of such an hypothesis appears to us to lead to difficulties of two kinds, the first arising out of the geometrical conceptions involved in it, and the second being met with in the attempt to extend it to other elements. It ascribes a perfectly distinct existence to these four bonds, so that in all carbon compounds we have to deal with neither more nor less than that number, unless we make the additional assumption that in certain cases the carbon-atom may lose its tetrahedric character.

And farther, if the tetrahedric relation of the valencies is unvarying, it is difficult to conceive in what way the atom can be united by more than three of its bonds to one atom of any other element.

We meet then with the difficulty of having to explain the existence of such compounds as carbonic oxide, in which carbon appears to be no longer quadrivalent, or of certain cyanogen compounds, as for example the isocyanides in which the carbon-atom is either combined by more than three bonds to a single nitrogen-atom or is bivalent,  $R'N=C$  or  $R'N\equiv C$ : so that in attempting to remove the one objection, we are brought face to face with the other, namely, that *ex hypothesi* we conceive the valency of each element to be constant. Such instances are rare in comparison with the number of bodies which fall in with the hypothesis of Van t' Hoff, but they are well known and well defined. We do not, however, dwell further on this subject, hoping to attack it experimentally later, merely stating here that results we have obtained with the nitrogen-atom bear also on this matter.

Willgerodt has brought forward the view that the nitrogen-atom may be regarded as having a configuration represented by a double tetrahedron. We have given some attention to the question of the



configuration of the atoms possible in the case of several elements and among them more particularly of nitrogen, and we have come independently to the same conclusion and have endeavoured to put the hypothesis to the test of experiment.

Starting from the consideration that a nitrogen-atom combined with four or five different groups should give a compound capable of isomerism, and that among these isomers there are two possible, the form of one of which is the non-superposable image of the other, we have attempted to obtain such a body containing what is in fact an "asymmetric nitrogen," and capable, one would suppose, of rotating the plane of polarisation to the right or to the left. The separation of these isomers, if they exist, we have not yet succeeded in effecting.

Attacking the problem from another point of view we find that a space configuration such as that given above requires that we consider nitrogen as essentially a quinquivalent or pentad atom. We have then to reconcile with this view the fact that nitrogen in a large number of cases appears to be triad.

We have endeavoured to find an explanation in the supposition that one atom of nitrogen in its apparently triad condition may combine by its two available affinities with another similar atom to form a condensed molecule, and that such molecules are readily dissociated by heat into the ordinary molecules containing quasi-triad nitrogen.

To test the hypothesis, we measured the expansion of a known quantity of amine vapours when the temperature was raised from that of the laboratory to  $100^{\circ}$ , the pressure remaining constant.

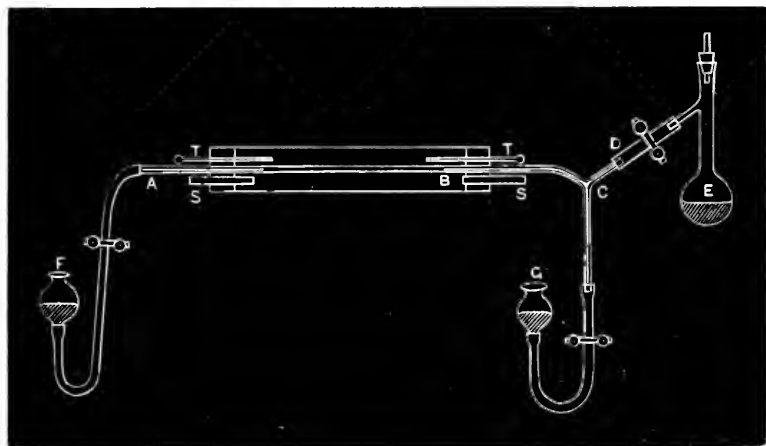
The apparatus used consisted of a horizontal tube, AB, about 700 mm. long and 2.5 mm. in the bore, to which was attached the T-piece C of the shape shown in the figure. To A and C were fitted rubber tubes with mercury bulbs, F and G, which could be raised or lowered as required. To the end D was attached the distillation bulb E containing the substance to be experimented upon in the liquid state; and this again was connected with a Sprengel pump. The tube AB was enclosed in a glass jacket provided with two thermometers, T, and tubes, S, for the supply and exit of steam.

The apparatus having been partially exhausted, the mercury was caused to fill the tube AB completely by raising the reservoirs F and G. The clamp on F having been tightened, G was lowered and raised repeatedly, so as to ensure the expulsion of the air from the connections and the replacement of it by the amine vapours.

Then G having been lowered till the mercury stood just below the bend of the T-piece, F was lowered so as to draw over some of the vapour into the tube AB. Then F was clamped, and the Sprengel pump worked till the mercury from G rose up the branch D.



When this was done, the clamp at D was screwed tight, and F lowered until the mercury from C reached a convenient fixed point, B, in the horizontal tube within the steam jacket.



Thus any possible condensation of the saturated vapour was avoided, the pressure on the enclosed gases being less than when they were drawn in. To make sure of this, however, the length  $V_0$  of the column of gas was finally increased by about 50 per cent. by simultaneously lowering F and G. It may be noted here that condensation was at once evident on increasing the pressure after the gas was enclosed. Lastly, the clamp on F was tightened, and the volume of the gas taken by measuring the length  $V_1$  of the column enclosed in the horizontal tube, the thermometers being read at the same time.

Next, steam was passed into the jacket. During the heating, the mercury bulb F was lowered, and the clamp slackened to permit the gases to expand; when the temperature was again steady, the pressure was finally adjusted so as to bring the column at B to exactly the same mark as before, all the adjustments being performed with F, so that neither the bulb C, nor the clamp upon its tube, was touched during the whole experiment. After measuring the volume  $V_2$  at this higher temperature, as a further check upon the results the pressure in G was again lowered in some experiments, and the mercury brought back by means of F to its original position at B, and the increased volume  $V_3$  once more taken.

Lastly, the steam was turned off, the apparatus allowed to cool, and a final measurement of the volume  $V_4$  at the temperature of the laboratory was made.

It will be observed that the horizontal direction of the column of mercury at its upper extremity, and the fixed position of the bulb G, enabled us to secure with great accuracy the same pressure for each pair of measurements. The smallness of the volume operated upon is, however, an objection which will be remedied in our next apparatus.

Several blank experiments were first made with air to test the accuracy of the method, and the average error was found not to exceed 0.5 per cent. in the expansion between 17° and 100°.

Then we introduced various amines into the bulb E, and now obtained on heating an expansion of 5 or 6 per cent. above the normal.

Next, we substituted ether vapour for the amines when the abnormal expansion to a great extent disappeared—though not completely. This we ascribed to the difficulty of freeing the apparatus of the amines, the scent of which hung about the rubber connections in spite of repeated exhaustions. Finally, we operated on a solution of pure monethylamine in ether dried over potash, when the abnormal expansion re-appeared.

The equivalence of  $V_0P_0$  to  $V_1P_1$  at the temperature of the laboratory, and of  $V_2P_2$  to  $V_3P_3$  at 100° proved that at each of these temperatures the vapour of the amines obeys Boyle's law; while the equivalence of  $V_1P_1$  to  $V_4P_4$  showed that the heating caused no permanent increase of volume. But a comparison of  $V_1, P_2, t_1$  and  $V_2, P_2, t_2$  showed that there was an increased expansion of the amine vapours which was not observed in the case of air or ether.

The following are some of the results:—

No. 1.—*Test Experiment with Air.*

Pressure = 264 mm.

Volume at 13.5° .....  $V_1 = 199.0$

Volume at 100° .....  $V_2 = 257.7$  observed.  
259.08 calculated.

Here the error is about  $\frac{1}{2}$  per cent.

No. 2.—*Mixture of Mono-, Di- and Tri-ethylamine in Aqueous Solution.*

Pressure = 148 mm.

Volume at 15° .....  $V_1 = 159.0$

Volume at 100° .....  $V_2 = 234.0$  observed.  
205.9 calculated.

This experiment gave an abnormal expansion of about 12 per cent.

No. 3.—*The same as in No. 2.*

Pressure = 383 mm.

Volume at 15° .....  $V_1 = 148.0$

Volume at 100° .....  $V_2 = 207.25$  observed.  
191.68 calculated.

Pressure lowered to 263 mm.

Volume at 100° .....  $V_3 = 300$

$V_2P_2 : V_3P_3 = 78898 : 78900.$

The abnormal increase was about  $7\frac{1}{2}$  per cent., but the pressure was not so low.

No. 4.—*The same Mixture of Amines dried over Potash.*

Pressure = 173.5 mm.

Volume at 13.5° .....  $V_1 = 121.0$

Volume at 100° .....  $V_2 = 167.0$  observed.  
157.5 calculated.

On cooling, volume at 17 = 122, *i.e.*, = 120.53 at the original temperature. Abnormal expansion of 6 per cent., with return to the original volume within the instrumental error.

No. 5.—*The same as No. 4.*

Pressure not noted, but about 250 mm.

Volume at 16.5° .....  $V_1 = 183.0$

Volume at 100° .....  $V_2 = 250.0$  observed.  
235.8 calculated.

Abnormal expansion of 6 per cent.

No. 7.—*Monethylamine in Aqueous Solution.*

Pressure 398.5 mm.

Volume at 17° .....  $V_1 = 200$

Volume at 100° .....  $V_2 = 272$  observed.  
257 calculated.

Abnormal expansion of nearly 6 per cent.

No. 8.—*Test Experiment with Ether Vapour.*

Pressure = 389 mm.

Volume at 17° .....  $V_1 = 195.0$

Volume at 100° .....  $V_2 = 253.5$  observed.  
250.4 calculated.

Error about 1.2 per cent.; but the mercury smelt of ethylamine.

No. 9.—*Test Experiment with Ether after Continuous Exhaustion and Heating of the Tube.*

Pressure 697 mm.

Volume at 15.0,  $V_0 = 135$        $V_0P_0 = 94095$

Pressure 452 mm.

Volume at 15.5,  $V_1 = 209$        $V_1P_1 = 94120$

Pressure 452 mm.

Volume at 100.5,  $V_2 = 278$        $V_2P_2 = 125755$

Pressure 363 mm.

Volume at 100.5,  $V_3 = 347$        $V_3P_3 = 125961$

Observed volume at 100.5 = 278

Calculated                      „                      = 271

The error was larger than in the previous case; but after the experiment, on cooling down to 17°, the observed volume was within 1 per cent. of the calculated, and the mercury still smelt strongly of the amine.

No. 10.—*Monethylamine Dissolved in Ether, dried over Potash.*

Pressure = 379.5 mm.

Volume at 17° . . . . .  $V_1 = 200.0$

Volume at 100° . . . . .  $V_2 = 267.0$  observed.  
257.2 calculated.

Pressure 291.5 mm.

Volume at 100° . . . . .  $V_3 = 349.5$

Volume at 18° . . . . .  $V_4 = 263.5$

Relation of final volume at 18° to original volume at 17° reduced to same temperature and pressure = 1 : 1013583.

The relations  $V_0P_0 : V_1P_1$  at 15° and  $V_2P_2 : V_3P_3$  at 100° also varied only by about 1 per cent.

The abnormal expansion was in this case nearly 4 per cent. between 17° and 100°.

The above experiments seem to show that to some extent, at least, the vapour of ethylamine breaks up when heated from 17° to 100° into a larger number of molecules. Similar abnormal expansion has been observed in bodies which must be regarded as completely saturated in the single molecule—but in all these cases polymerisation is

structurally possible, and we think that in the nitrogen compounds it is necessary, if we are to extend Van t' Hoff's hypothesis to them.

Wurtz, who investigated methylamine and ethylamine (*Ann. Chim. Phys.* [3], 30, 467) was unable by ordinary means to determine their vapour-density.

Izarn, to whom he referred the matter, employing a new method, measured the vapour-density of the two amines at different temperatures and pressures, and found in every case a greater value than that required by theory. Thus, at  $35.84^{\circ}$  and 1128 mm., the density of ethylamine was 1.6027 observed, as against 1.5568 calculated. Izarn, however, did not experiment at temperatures lower than  $27^{\circ}$ , or higher than  $56^{\circ}$ . Our own observations made at pressures of from  $\frac{1}{6}$ th to  $\frac{1}{3}$ rd of that employed by him in the experiment quoted, by showing an abnormal expansion to take place on raising the temperature from  $17^{\circ}$  to  $100^{\circ}$ , seem to indicate that the specific volume of the vapour is a function not so much of the pressure as of the temperature, and it is on this that the hypothesis which we now put forward is founded.

The equality of the four valencies of carbon, which has been sufficiently established by experiment, is well represented by the symmetry of the tetrahedron, and we must suppose that a rise of temperature affects them all equally. Carbon, therefore, unless in combination with an element which is not symmetrical in its space relations, must be tetrad at all temperatures. This property it can only have in common with those elements which can be represented by the five regular solids, the valencies of which *ex hypothesi* must be 4, 6, 8, 12, and 20, corresponding to the number of the solid angles of those bodies. It is impossible, therefore, to find a geometrical representation for diad, triad, and pentad atoms which shall be symmetrical in three-dimensional space, and it becomes almost a necessary consequence of Van t' Hoff's hypothesis when we attempt to extend it to the nitrogen-group, that we should have two of the valencies different in value from the other three. Moreover, this difference would be manifested above a certain critical temperature, but would probably disappear below it, and, further, the union of an element of strong affinity with one of the valencies might render the other four equal with respect to atoms of weaker affinity.

With regard to the latter supposition, representing the pentad atom by a double tetrahedron, if we suppose one angle taken up, for instance, by chlorine, the remaining four are symmetrically situated with respect to one point within the atom, and may be saturated by four equal atoms or groups as in the ammonium, phosphonium, and arsonium salts.

The effect of certain elements in weakening the bonds of other

elements is a matter of ordinary observation (see Van t' Hoff, "*La Chimie dans l'espace*"). Compare, for example, the relative strength of the affinity between two carbon-atoms when combined with hydrogen, oxygen, or nitrogen, *e.g.*,  $\text{CH}_3\text{—CH}_3$ ;  $\text{CH}_3\text{—COOH}$ ;  $\text{COOH—COOH}$ ;  $\text{CH}_3\text{—CN}$ ;  $\text{CN—CN}$ .

Again, the action of heat in weakening chemical affinity is also a matter of common experience. Thus, mercury, cadmium, and zinc in the gaseous state have no affinity in respect to atoms of the same kind, whilst iodine vapour exhibits the same phenomenon at high temperatures.

Now, as regards the nitrogen-atom, it appears that in contrast to carbon it is the hydrogen and hydrocarbon groups which weaken the affinity between nitrogen-atoms. Thus, we have  $\text{NO}_2\text{—NO}_2$ , but not  $\text{NH}_4\text{—NH}_4$ , nor  $\text{NH}_3\text{=NH}_3$ , at ordinary temperatures.

Hence, in the case of the amines, the bonds uniting the nitrogen-atoms in the double molecule will probably be extremely weak, and likely to be destroyed even at a comparatively low temperature. It is interesting in this connection to recall the fact that Hofmann (*Ber.*, 3, 112) found that it was practically impossible to separate the three ethyl bases (mono-, di-, and tri-ethylamine) by distillation, in spite of there being an interval of some  $40^\circ$  between the boiling points of ethylamine and diethylamine, as well as between those of diethylamine and triethylamine. Now, it is conceivable that in such a mixture a molecule of one amine may unite with a molecule of a different amine to form a compound more stable than if both molecules were precisely similar, and capable accordingly of being volatilised to a certain extent without being dissociated.

In conclusion, we would say that, in our opinion, the nitrogen-atom is essentially pentad, and that when we find it triad we have to deal with molecules which have been dissociated, and in which the two available bonds of the nitrogen-atom are too feeble at the temperature of observation to enable two molecules to hold together.

We hope to continue our experiments as to the valency and space configuration of the nitrogen-atom and other atoms.

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LXV.—*The Resin of Myoporum Platy-  
carpum.*

By J. H. MAIDEN, F.L.S., Curator of the Technological Museum,  
Sydney.

A VERITABLE natural sealing-wax is yielded by a small tree which is found in the interior of Australia; it occurs in the more arid portions of all the colonies, except Queensland. The tree is *Myoporum platycarpum*, R. Br., and it possesses a variety of local names, such as "Sandalwood," "Dogwood," and "Sugar tree;" the latter because a manna exudes from it which is greedily sought after by the blacks, and is likewise much appreciated by colonists. It yields a resin, which is used by the aborigines as a substitute for pitch and wax; for example, they use it either alone, or mixed with fat, to cement the stone heads of their tomahawks to the fibre which joins them to the stick forming the handle. As has been already hinted, it forms a natural sealing-wax, and is sometimes used by people in the interior for this purpose. It would probably serve as a constituent of black sealing-wax; alone it is too soft for keeping in this climate.

It sometimes occurs in great quantities on the stem, is hard and brittle, breaks with a glassy fracture which is at first of a purple or indigo colour, but becomes brown on keeping. Often it may be picked up from under the trees in rounded or globular pieces.

Two samples have come into the writer's hands, and a few notes concerning them will doubtless be interesting. The first, from the Lachlan River, New South Wales, is in small rounded lumps usually weathered on the outside, and having a pleasant empyreumatic odour; these are of a dark reddish-brown colour, fly with the slightest touch of the pestle, and are easily powdered. The resin has a bright fracture, which appears almost black, but shows reddish-brown at the edges. It softens even with the warmth of the hand, and if kept in a bottle, the heat of an average summer day is sufficient to fuse pieces presenting fresh fractures.

It presents some external resemblance to guaiacum resin (especially when that substance comes to market in small lumps), but it is not so green in colour as the latter. It has no taste. Cold water has no effect on it, but if the water be heated the resin melts and floats, forming a liquid much resembling tar, but of a purplish-brown colour. The water remains clear, colourless and almost odourless.

Light petroleum dissolves 46·8 per cent. of a reddish-brown resin, destitute of odour. Alcohol dissolves from the residue 28·1 per cent.

of a deep reddish-brown resin, which is almost black by reflected light.

The residue was boiled in water and 1·7 per cent. of saline matter was extracted, while 23·4 per cent. of accidental impurity was left behind. This is of a chocolate colour, and under a lens was seen to consist of a little ligneous matter, with a large percentage of inorganic impurity. It was quite free from gum.

*Summary.*

$\alpha$ -Resin soluble in light petroleum .....	46·8
$\beta$ - „ „ alcohol .....	28·1
Saline matters .....	1·7
Accidental impurity.....	23·4
	<hr/>
	100·0

The crude resin melts at 90·5°. It contains no tannic acid.

The second sample was procured from Netallie, Wilcannia, New South Wales. It presents no marked points of difference, as regards physical appearance, from the preceding one. On treating it with alcohol, the liquid is not so dark as that yielded by the preceding sample, neither is the colour so rich. It resembles tawny port, but is a little darker.

Light petroleum extracts 48·6 per cent. of resin, and alcohol added to the residue extracts 36·4 per cent.

LXVI.—*The Lowering of the Freezing Point of Sodium by the Addition of other Metals.*

By C. T. HEYCOCK, M.A., and F. H. NEVILLE, M.A.

IN a preliminary note communicated to the Society on March 21st, 1889, and published in the Proceedings, No. 65, p. 41, we drew attention to the lowering of the freezing point of tin produced by the addition of small quantities of other metals. Since then we have examined the behaviour of alloys of tin with sodium, gold, bismuth, and thallium, and have re-examined zinc through a long range. The accompanying table gives a summary of our results, using tin as a solvent.



TABLE I.—*Fall produced in the Freezing Point of Tin by dissolving one Atomic Weight of Metal in 100 Atomic Weights of Tin (that is 11,800 parts).*

	Melting points (Carnelley).	Atomic weight.	Atomic fall.	
Sodium .....	95·6	23	2·5	Different examples of Al used.
Aluminium ....	700·0	27	1·34	
Copper .....	1054·0	63	2·47	
Zinc .....	433·0	65	2·53	
Silver.....	954·0	108	2·67	
Cadmium .....	320·0	112	2·16	
Antimony.....	432·0	120	rise 2·3	
Gold .....	1045·0	197	2·80	
Mercury .....	30·0	200	2·3	
Thallium. ....	294·0	203	2·6	
Lead .....	326·0	208	2·6	
Bismuth .....	268·0	210	2·10	

In a future communication we hope to give full details of these experiments, and to show to what extent these atomic falls remain constant with increasing concentration.

#### *Sodium as a Solvent.*

*Method of Experiment.*—The crucible in which the solvent was melted, except where otherwise stated, consisted of a cylinder of cast iron, 6—8 inches high, and 5 inches diameter. In the axis of this cylinder a hole was bored, from 1—2 inches diameter, and about 4 inches deep. Within this hole, an annular iron stirrer worked up and down by means of a small water motor—both the length of stroke of the stirrer and its rate of motion could be varied. The block rested on a double ring gas burner, and its rate of cooling was controlled by the use of asbestos cloth wrappings and covers. The rate of cooling was usually about a degree in two minutes.

The thermometer, made by Mr. Hicks of Hatton Garden, was graduated in an arbitrary scale of millimetres, 10 mm. corresponding nearly with 1° C. As the readings were all made with a telescope, the temperatures could be read to nearly  $\frac{1}{100}$ th of a degree. The zero of this thermometer had been fixed by long annealing in oil according to the method Mr. Hicks adopts; this precaution, though not so necessary for low temperatures, is indispensable for working at

high temperatures. When tin is used as a solvent, the zero of common thermometers changes during the course of a few hours.

The bore of the thermometer was carefully calibrated, and found to be slightly conical; the correction due to this was plotted, and has been applied to all the temperatures we give, but we have accepted the fixed points sent with the thermometer, so there may be a small  $\pm$  error which, owing to the nature of the experiments, is unimportant. During the experiments, the thermometer was clamped in the axis of the cylinder, and raised about a millimetre from the bottom of the hole, so that the stirrer worked round it along the whole length of the bulb. In making an experiment, solid paraffin was first placed in the crucible, and then a weighed quantity of sodium from 20—30 grams (in large sticks) was dropped in, the molten paraffin forming a layer about 0.5 inch thick above the sodium prevented loss by oxidation or splashing. The crucible was raised well above the melting point of sodium, and allowed to cool slowly whilst constantly stirred.

The thermometer was always observed to fall steadily, and then suddenly to rise through a short range of temperature from 1—2° C., it then remained stationary for several seconds or even a minute.

The highest temperature reached during this surfusion was taken to be the *freezing temperature* of the metal or alloy; determined in this way, the freezing points of most alloys are extremely constant.

At temperatures near its freezing point, and even up to 250°, sodium, unlike tin, dissolves only a few metals; thus, Au, Li, K, Hg, Tl, and In dissolve freely, Pb and Cd very sparingly, whilst we have not succeeded in dissolving at present appreciable quantities of other metals, such as Zn, Sn, Al, Mg, Ag, Pt, Fe. Tin even when fused with sodium fails to give a true solution.

The method adopted for testing the solubility of metals was to fuse the sodium under paraffin in a test-tube, and then to add small quantities of the metal in fine division, the temperature being raised to the boiling point of the paraffin. When cold, a clean piece of the sodium was thrown into absolute alcohol when any dissolved metal separated out in a fine powder, generally in minute crystals.

#### *Effect of Gold on the Freezing Point of Sodium.*

Ignited precipitated gold dissolves very readily at temperatures a few degrees above the melting point of sodium. The freezing point after each addition of gold was determined twice, the temperatures rarely showed a difference of a tenth of a millimetre.

TABLE II.—*Gold in Sodium.* 1st Series.

Expt. number.	Wt. Na.	Wts. of Au added in succession.	Temps. of freezing point in ° C.	Atoms of Au per 100 atoms Na.	Atomic fall.	Remarks.
(1)....	26·00	—	97·47	—	—	
(2)....	"	0·2536	96·85	0·1138	5·45	
(3)....	"	0·1895	96·51	0·1989	4·87	
(4)....	"	0·2157	96·07	0·2957	4·74	
(5)....	"	0·3168	95·39	0·4514	4·61	
(6)....	"	1·1438	93·09	0·9655	4·536	
(7)....	"	0·8844	91·29	1·363	4·535	
(8)....	"	0·6522	89·96	1·6562	4·535	
(9)....	"	1·0145	87·91	2·1122	4·525	
(10)....	"	0·9388	86·07	2·5313	4·5	F. P. rather uncertain until a nucleus of solid alloy was used to determine solidification.
(11)....	"	1·0352	83·89	3·0	4·53	
(12)....	"	1·008	81·92	3·453	4·515	
(13)....	"	0·9630	82·1	—	—	Temperature remained stationary till whole alloy solidified.
(14)....	"	0·261	82·0	—	—	Raised to 155 .
(15)....	"	0·481	82·1	—	—	

## 2nd Series.

(1)....	20·425	—	97·14	—	—
(2)....	"	2·1	91·99	1·2	4·51
(3)....	"	1·316	88·59	1·953	4·53
(4)....	"	3·067	82·1	3·705	4·14
		6·483			

Sodium being now more than saturated with gold, additional sodium was added to dilute the solution.

(5)....	23·565	"	82·99	3·211	4·50
(6)....	25·160	"	83·99	3·022	4·45
(7)....	27·205	"	85·03	2·781	4·46
(8)....	29·86	"	86·14	2·534	4·46
(9)....	31·705	"	86·5	2·390	4·43
(10)....	35·015	"	87·75	2·161	4·48
(11)....	39·025	"	88·75	1·94	4·48

100 atomic weights of sodium will therefore keep in solution about 3·5 atomic weights of Au. Hence this represents the fully saturated solution of gold in sodium. The behaviour of a solution of gold in sodium appears to be very like that of a weak solution of sodium chloride in water (*cf.* Guthrie, *Phil. Mag.* [4], 46).

The minimum temperature of  $81.92^{\circ}$  is singularly constant when reached, remaining stationary until the whole mass has solidified.

*Properties of the Sodium Gold Alloys.*

When the alloys are treated with alcohol, gold is precipitated in very fine needles. In appearance, the solid alloys resemble sodium, though slightly whiter in colour. They are somewhat harder to cut with a knife than ordinary sodium, and the cut surfaces oxidise much more rapidly, probably owing to the action on the moisture of the air of the couple formed by the gold and sodium.

An alloy obtained by diluting with sodium the fully saturated sodium and gold alloy solution was analysed by adding weighed portions of the alloy to alcohol, titrating with normal HCl for sodium, washing, and weighing the gold.

Two analyses gave a mean result—

	Found.
Au . . . . .	15.00
Na . . . . .	85.03
	<hr/>
	100.03

It appeared of interest to ascertain whether this alloy would remain homogeneous when kept fused for some time, notwithstanding the enormous difference in the densities of gold and sodium.

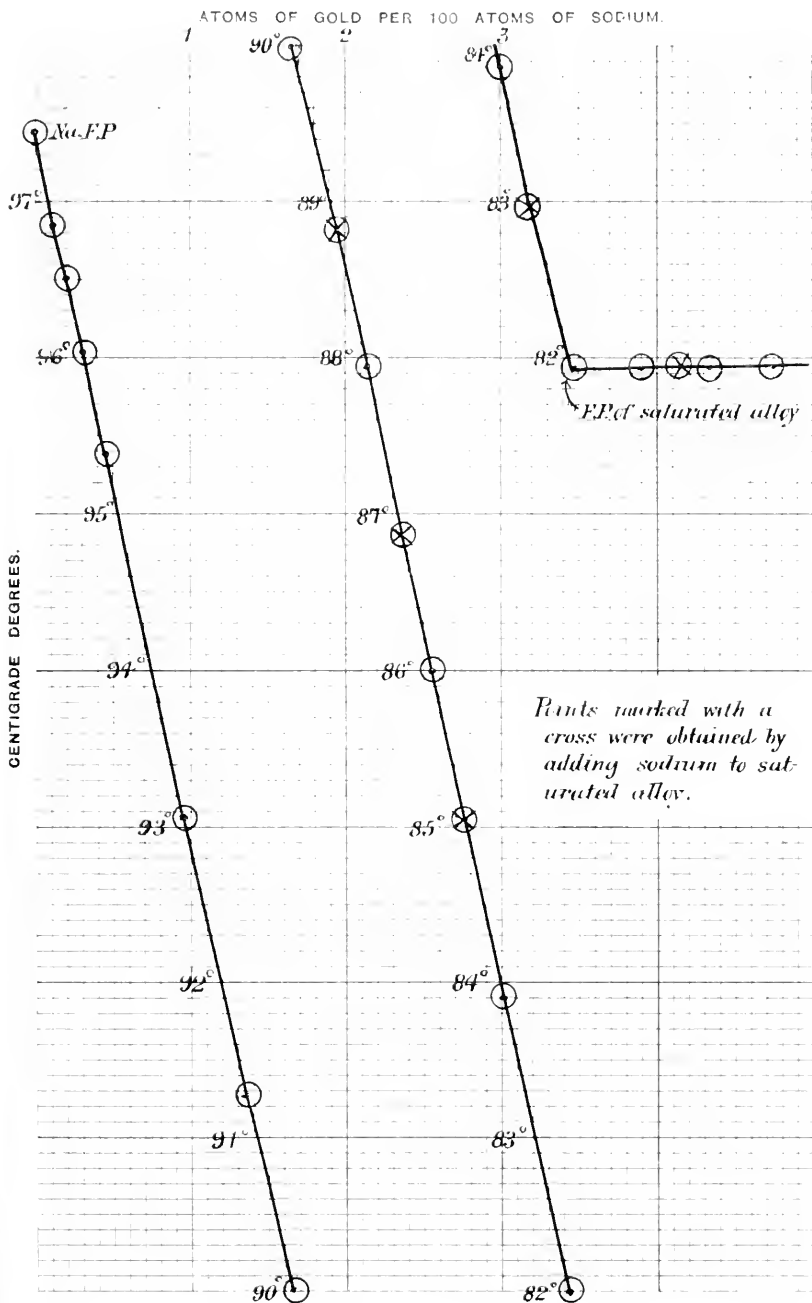
For this purpose a test-tube was filled with the alloy, and kept at  $130^{\circ}$  for 48 hours under paraffin; it was then rapidly cooled, and after solidification portions were cut off from each end of the cylinder (which was about 4 inches long), and analysed as before.

		Found.	Calculated from weights of Na and Au used.
Top of cylinder,	Na . . . .	85.33	85.75
" "	Au . . . .	14.16	14.25
		<hr/>	<hr/>
		99.49	100.00
Middle of cylinder,	Na . . . .	84.89	
" "	Au . . . .	14.60	
		<hr/>	
		99.49	
Bottom of cylinder,	Na . . . .	84.49	
" "	Au . . . .	14.60	
		<hr/>	
		99.49	

The defect in each case is due to traces of paraffin intermixed with

# FALL IN THE FREEZING POINT OF SODIUM PRODUCED BY ADDING GOLD.

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the alloy. It thus appears that when fused no separation of the metals takes place.

The relative density of this alloy taken in naphtha was found to be 1.152; assuming the composition to be Na 85 per cent., Au 15 per cent., and that no change of volume takes place on mixing, the calculated density is 1.141. Hence the density of the alloy is a mean of the densities of its components, which perhaps indicates that the solid alloy is a mixture. This view is borne out by the comparatively large size of the crystals of gold which separate out when the alloy is treated with alcohol. As the full investigation of the physical and chemical properties of this alloy would have taken us away from our main subject, we defer the repetition and further verification of these results for a future paper.

TABLE III.—*Thallium dissolved in Sodium.*

Expt. num-ber.	Wt. Na taken.	Wts. of thallium added in succe-sion.	Freezing point of solution.	Number atoms Tl per 100 atoms Na.	Atomic fall.	Remarks.
1. ....	22.53	—	97.46	—	—	
(2)....	„	0.3277	96.81	0.164	3.93	
(3)....	„	0.4865	95.81	0.408	4.044	
(4)....	„	0.3525	95.04	0.635	3.81	
(5)....	„	0.3355	94.34	0.753	4.143	Na raised to 180° be-fore adding this por-tion of Tl.
(6)....	„	0.6515	93.05	1.033	4.269	
(7)....	„	0.6620	91.65	1.41	4.120	
(8)....	„	1.8915	87.3	2.36	4.728	Raised to 150°.
(9)....	„	1.561	83.64	3.14	4.401	
(10)....	„	1.280	80.745	3.783	4.683	
(11)....	„	1.2015	77.87	4.384	4.468	Raised to 145°.

Thallium dissolves in sodium very readily, as it is only necessary to raise the sodium about 20° above its freezing point to dissolve rapidly a lump of thallium weighing a gram or so. The extent to which this lowering is continued has not yet been determined, as we have not at present a thermometer with a sufficiently open range.

It is remarkable that thallium which is so nearly related to the alkalis on the one hand is readily soluble in sodium, whilst lead, the other element to which it is nearly equally closely allied, is almost insoluble in sodium.

When the mercury was added to the molten sodium, a considerable evolution of heat and light took place. It is worthy of

TABLE IV.—*Mercury dissolved in Sodium.*

Expt. num-ber.	Wt. Na taken.	Wts. of Hg added in succession.	Freezing point of solution.	Number of atoms of Hg per 100 atoms Na.	Atomic fall.	Remarks.
(1)....	32.47	—	97.47	—	—	Raised to over 200°
(2)....	„	0.5605	96.6	0.1986	4.38	
(3)....	„	0.7410	95.38	0.4609	4.534	
(4)....	„	0.5740	94.46	0.6643	4.531	
(5)....	„	0.5170	93.64	0.847	4.519	
(6)....	„	1.771	90.93	1.475	4.43	
(7)....	„	4.950	83.35	3.228	4.374	
Another Series.						
(1)....	20.13	—	97.49	—	—	
(2)....	„	0.5859	95.95	0.335	4.6	
(3)....	„	1.4938	92.25	1.189	4.4	

TABLE V.—*Mixture of Thallium and Mercury dissolved in Sodium.*

Expt. num-ber.	Wt. of sodium added suc-cessively.	Wt. of thallium added suc-cessively.	Freezing point of solution.	Number of atoms Tl per 100 Na.	Total number of foreign atoms.	Atomic fall.
					Hg + Tl.	
(1) .....	20.13 + 2.08 Hg.	—	— 92.25°	— —	— —	— 4.4 due to Hg.
(2) .....	„	1.0425	89.86	0.585	—	4.09 due to Tl.
(3) .....	„	1.163	86.97	1.237	—	4.27 due to Tl.
(4) .....	+ 7.53 (total Na 27.66).	—	90.10	0.9006	1.765	4.19 due to both Tl and Hg.
(5) .....	„	0.8205	88.61	1.235	2.136	4.16 due to both Tl and Hg.
(6) .....	„	1.27	86.29	1.795	2.66	4.20
(7) .....	„	1.122	84.2	2.252	3.117	4.26 due to both Hg and Tl.

note that the atomic falls do not indicate in any way the formation of a chemical compound as might be anticipated. Had the mercury after addition appropriated a portion of the solvent, it should have made these atomic falls (?) increase as the number of atoms of solvent



diminished. It seems not unreasonable to suppose that a compound may be formed at first and dissociated afterwards through the great dilution of the solution.

At present we have made scarcely any experiments with mixtures of three elements.

To the solution of mercury in sodium, Table IV (Experiment 10), thallium was added.

TABLE VI.—*Cadmium dissolved in Sodium.*

Expt. number.	Wt. Na taken.	Wt. of cadmium added in succession.	Freezing point of mixture.	Number of atoms of Cd per 100 atoms Na.	Atomic fall.	Remarks.
(1).....	21.07	0.0	97.49°	—	—	
(2).....	"	0.0995	97.11	0.0969	3.92	Raised to 260°.
(3).....	"	0.102	96.75	0.1964	3.74	Raised to 260°.
(4).....	"	0.0940	96.42	0.288	3.72	
(5).....	"	0.1055	96.04	0.3908	3.71	
(6).....	"	0.0792	95.83	0.4681	3.55	
(7).....	"	0.078	95.54	0.5441	3.584	Raised to 240°.
(8).....	"	0.106	95.431	0.6475	3.173	Raised to 249° before determination of freezing point.
(9).....	"	0.194	95.43	0.8365	—	Raised to 260° before determination of freezing point.

Cadmium dissolves but slowly in sodium, and it is necessary to raise the temperature after each addition of cadmium very considerably.

The table shows that the solution became fully saturated at the temperature of 95.43° when it contained 0.7642 gram of cadmium (total weight added, experiments 2—8 inclusive), that is, 3.05 per cent. cadmium.

Beyond this, further addition of cadmium ceases to produce any effect.

The introduction of small masses of potassium is attended with almost unavoidable loss by oxidation. This was diminished as far as possible by cutting the potassium in a deep basin into which a brisk current of dry carbon dioxide was passed; the potassium was then weighed in a tube full of carbon dioxide. We intend shortly to investigate further the action of potassium on sodium to see if the

lowering holds good for considerable percentages of potassium, especially the behaviour of the liquid alloy.

TABLE VII.—*Potassium dissolved in Sodium.*

Expt. number.	Wt. Na taken.	Wt. of K added successively.	Freezing point of solution.	Number of atoms K added per 100 atoms Na.	Atomic fall.
(1) .....	34·83	0·0	97·49°	—	—
(2) .....	„	0·160	96·52	0·2708	3·58
(3) .....	„	0·601	92·88	1·288	3·58
(4) .....	„	0·744	88·81	2·547	3·408
(5) .....	„	0·536	85·93	3·455	3·345

Another Series, using an Atmosphere of Nitrogen without Paraffin.

	75·9	0·0	97·14	—	—
	„	0·204	96·53	0·158	3·85
	41·87	—	97·5	—	—
	„	0·1023	96·99	—	3·45

#### *Silver in Sodium.*

Since silver even when finely precipitated (Stas' method) is practically insoluble in sodium at temperatures near its freezing point, an attempt was made to dissolve the silver in mercury and then to add this amalgam to the sodium. The silver would probably under these circumstances be in a favourable condition for solution.

20·64 grams sodium, freezing point 97·49°, were taken, and to this an amalgam of 0·201 gram of precipitated silver dissolved in 2·16 grams mercury was added. Freezing point of mixture 92·2° and 92·11°. Calculating the effect produced by the mercury alone (from Table IV), the lowering should have been 92·19. Hence we conclude that silver is insoluble in sodium, and that the amalgam behaved like a solution of a resin in alcohol when thrown into water, the silver being precipitated. Silver, even when heated strongly in a test-tube with sodium, did not dissolve.

#### *Zinc in Sodium.*

Zinc was treated in the same way, that is, by amalgamating with mercury, but like the silver in the foregoing experiment it produced no effect, the fall being almost exactly accounted for by the action of the mercury alone.

*Lithium in Sodium.*

Of all the metals, lithium, on account of its extremely low atomic weight, presents the greatest interest. Unfortunately, however, it is exceedingly difficult to work with in presence of sodium; even at 100° it oxidises with great rapidity and attacks the iron blocks. Further, on account of its very low specific gravity, it is impossible to use more than a film of paraffin over the sodium, otherwise the lithium floats, and never comes in contact with the sodium.

After the loss of a considerable portion of lithium, these difficulties were partly overcome by placing a wide test-tube in the iron block and melting the sodium in it. Through the cork of the test-tube the shaft of a glass stirrer, the thermometer, and a small tube were passed. A trace of paraffin was added, a good stream of nitrogen was then passed in, and the sodium raised above the melting point of lithium (180°). A weighed piece of lithium was then thrown in and rapidly stirred, and the temperature reduced as quickly as possible. The preliminary experiments are omitted as worthless.

TABLE VIII.—*Lithium dissolved in Sodium.*

Expt. number.	Wt. of Na taken.	Wt. of lithium added.	Freezing point of mixture.	Number of atoms of Li per 100 Na.	Atomic fall.
I.....	21·27	—	97·55°	—	—
II.....	"	0·0778	96·06	1·2	1·24
III.....	"	0·0348	95·46	1·74	1·11

*Lead in Sodium.*

Lead dissolves very sparingly indeed in sodium even when the temperature is raised considerably.

Thus 31·6 grams of sodium, f. p. 97·69°, after addition of 0·1215 gram of lead, had a freezing point 97·39°. This gives atomic fall of 4·6. Further addition of 0·1465 gram of lead produced no further fall in freezing point.

TABLE IX.—*Indium in Sodium.*

Expt. number.	Wt. of Na taken.	Wts. of In added in succession.	Freezing point of solution.	Number of atoms of In per 100 atoms of Na.	Atomic fall.
(1).....	23·0	—	97·6	—	—
(2).....	„	0·0303	97·51	0·0267	3·37
(3).....	„	0·0576	97·31	0·0774	3·75
(4).....	„	0·1472	96·32	0·2072	3·765
(5).....	„	0·2489	96·11	0·4267	3·49
(6).....	„	0·1370	96·09	—	—

To this saturated solution sodium was added.

	Wts. of Na added in succession.	Total indium present.			
(7).....	3·88	0·621	96·09	—	—
(8).....	1·43	„	96·1	—	—
(9).....	2·00	„	96·14	0·4155	3·51
(10).....	3·00	„	96·27	0·3783	3·51
(11).....	4·00	„	—	0·3376	3·55

Indium dissolves easily in sodium.

*Potassium as a Solvent.*

Potassium has been used for a few metals only. The atomic falls are approximately as follows:—Na 1·6, Au 1·8, Tl 1·7.

We intend to continue our researches, and hope to be able soon to communicate the results to the Society.

*Sidney College Laboratory,  
Cambridge.*

LXVII.—*The Alloys of Lead, Tin, Zinc, and Cadmium.*

By A. P. LAURIE.

IN a former paper ('Trans.' 1888, p. 88), I have described the behaviour of copper-zinc and copper-tin alloys in a voltaic cell, and deduced from their behaviour that the metals combine with one another, forming respectively a compound of the formula  $\text{Cu}_3\text{Sn}$  and  $\text{Zn}_2\text{Cu}$ .

The above metals are grouped together by Matthiessen as imparting to their alloys their physical properties in the proportion in which they are mixed one with another. It is, therefore, probable from this that they do not form compounds one with another, but are merely mixtures. If this view be correct, the electrometer should detect the more positive metal when the alloy is used in the voltaic cell in place of the zinc plate, even though the quantity of the more positive metal present be very small.

The first alloys experimented on were the lead-tin alloys. Unfortunately there is very little difference in potential between lead and tin, and it was necessary in consequence to use ten cells in series.

The alloys were made of the best grain tin and of assay lead, well mixed and cast in an iron mould in the form of thin plates. The cell used consisted of the plate of alloy, a slightly acid solution of stannous chloride, and a lead plate coated with lead chloride.

The alloys made up contained (*a*) 1 per cent. of lead; (*b*) 10 per cent. lead; (*c*) 50 per cent. lead; and (*d*) 70 per cent. of lead.

The E.M.F.'s obtained were as follows:—

Pure tin 0.035 volt; (*a*) alloy 0.015 volt; (*b*) alloy 0.020 volt; (*c*) alloy 0.015 volt; (*d*) alloy 0.015 volt.

It will be seen from this table that, whilst the introduction of 1 per cent. of lead modified the E.M.F. of the cell, the introduction of more lead had no further effect, and that there is therefore no evidence as far as the electrometer can show of the existence of a compound between lead and tin.

While testing the E.M.F. of these alloys, it seemed of some interest to determine afresh the alloy of lowest melting point, and study the distribution of lead and tin in blocks of alloys slowly cooled.

To determine the lowest melting point, some 800 grams of 50 per cent. alloy were allowed to cool, and the mother-liquor poured off from the crystals formed. This was done on two separate occasions, and the resulting alloy analysed: the first having 60.2 per cent. of tin, the second 60.4 per cent. of tin, giving a mean of 60.3 per cent.

of tin. This lowest melting point alloy is usually called in the text-books  $\text{Sn}_3\text{Pb}$ , which would give it a composition of 63.1 per cent. of tin. It will be seen that its composition does not really agree with any definite formula, although near enough to account for the assumption that it had one. (Tin has been taken as 118 in these calculations.) To determine the distribution of the metals on cooling, a square block of bees-wax  $1\frac{1}{2}$  inches in the side was bedded in a mass of plaster of paris and sand, two holes being left to the outside; the wax was then melted out and the alloy, after thorough mixing, run in. Two holes, one across, the other up and down, were then drilled through the block; the turnings were collected as they came out and analysed. In subsequent experiments the corners and centre of the block merely were analysed.

The results are given below. It will be seen that, though somewhat irregular in composition, a general tendency is apparent for the tin to be thrown to the outside of the block.

Only one alloy seems to be homogeneous, namely, that corresponding to 21 per cent. of tin. This is the lowest point of the density curve as given by other experimenters.

(1.) Alloy made up for 21 per cent. of tin. Analysis of borings in order through the block sideways, 20.10, 19.98, 20.09, 20.01, 20.03, 20.06, 20.04 per cent. From bottom to top of block, 20.06, 20.06, 20.04 per cent.

(2.) Alloy made up for 50 per cent. of tin. Analysis of the corners gave: for the top, 51.9, 50.21, 49.4, 50.5 per cent. of tin; for the bottom, 50.32, 50.03, 50.7 per cent. of tin. Analysis of the centre gave 48.95 per cent. of tin.

(3.) Alloy made up for 64 per cent. of tin. Analysis of borings through the sides gave, in order, 63.72, 63.37, 59.1, 61.16, 62.4, 63.6 per cent. Analysis from bottom to top, 62.2, 63.5, 64.1 per cent.

(4.) Alloy made up for 80 per cent. of tin. Top corners, 79.1, 79.95, 80.2, 80.2 per cent. of tin; bottom corners, 79.9, 79.4, 80.24, 80.3 per cent. of tin; centre of block, 73.2 per cent. of tin.

As confirming the result obtained by the electrometer, I may mention that Spring in a recent paper (*Bull. Acad. Roy. Belg.* [3], 11, 86) states that he does not believe that these metals form a compound. The usefulness of these alloys for wiping a joint is owing to their behaviour on cooling, one alloy apparently crystallising out after another, so that they remain in a pasty state for a considerable range of temperature.

The next alloys examined were the lead-zinc alloys. Matthiessen states that these metals do not even mix, the lead retaining only 1.7 per cent. of zinc. Some alloys were therefore made up containing 1 per cent. only of zinc, cast in thin plates, and tested on the

electrometer; the cell contained zinc chloride and lead plates coated with lead chloride.

The plates gave a deflection of 0.483 volt (zinc = .496 volt), thus indicating the presence of the 1 per cent. of zinc.

The plates were then scraped with a penknife and again tested. They now gave no deflection, showing apparently that all or nearly all the zinc lay in the outside portions of the alloy. On analysing the inside portion, it was found to contain only 0.4 per cent. of zinc.

Some fresh alloy was made up, cast in a circular form, and a thin layer removed in the turning lathe. This coating contained 2.4 per cent. of zinc, showing that the lead tries to reject even the 1 per cent. of zinc mixed with it. With reference to the failure of the electrometer to detect the 0.4 per cent., it may be pointed out that owing to local action a very minute trace of metal may be dissolved too quickly to show its presence; but this can always be remedied by amalgamating the plate.

Lead, then, apparently tries to reject every trace of zinc, and any zinc found in it may be regarded as mechanically caught in the metal while cooling.

The zinc-tin alloys were next tried in a cell containing zinc chloride, stannous chloride, and tin.

These metals seem to mix readily. The results are given below. The 1 per cent. alloy gave uncertain indications until amalgamated. Here again we have no indication of a compound.

Pure zinc, 0.536 volt. 1 per cent. zinc alloy, after amalgamating, 0.530 volt. The intermediate alloys containing 10, 50, and 70 per cent. of zinc gave similar deflections, showing that a small quantity of the more positive metal could be detected; the metals, therefore, do not combine.

Alloys of lead and 3 per cent. cadmium, and of tin and 3 per cent. cadmium were tested on the electrometer.

The E.M.F. of cadmium alone was 0.322 volt, that of the lead-cadmium was 0.264, and of the tin-cadmium 0.292 volt. Since, then, 3 per cent. of cadmium can be detected in either tin or lead alloys of the metal, we cannot suppose that cadmium combines with either of these metals.

The results of these experiments, then, is to show that the electrometer confirms the conclusions arrived at by Matthiessen, namely, that lead, tin, zinc, and cadmium do not combine with each other when mixed together. They also show the delicacy of the electrometer in detecting small quantities of more positive metals.

*Chemical Laboratory.*  
*People's Palace.*

LXVIII.—*The Magnetic Rotatory Power of Nitrogen Compounds, also of Hydrochloric, Hydrobromic, and Hydriodic Acids, and of some of the Salts of Ammonia and the Compound Ammonias.*

By W. H. PERKIN, Ph.D., F.R.S.

IN the previous investigations of the magnetic rotatory power of substances, in relation to their chemical composition, which I have had the honour of laying before this Society, my attention has chiefly been directed to compounds containing carbon, hydrogen, oxygen, and the halogens. This inquiry has now been extended, and in this communication an account is given of nitrogenous compounds. The object of this was to accumulate fresh facts, so as to get more material for generalisation, but more especially to study the influence of nitrogen upon the rotation of substances in which it exists in *tri*- and *penta*-valent conditions, because it has been repeatedly shown that compounds containing carbon in an unsaturated state have a considerably greater rotatory power than those in which it is saturated, and it therefore was a matter of interest to see whether other elements exerted a similar influence.

Substances of the following classes were examined in this inquiry: nitrates, nitro-compounds, nitrites, cyanides, ammonia, compound ammonias, and their salts.

With reference to the last-mentioned compounds, it was my original intention to examine the hydrochlorides or chlorides only, but, as these gave peculiar results, it was considered desirable to include ammonium bromide and iodide, and, for further comparison, ammonium nitrate and its sulphates; this made it necessary not only to determine the rotation of the salts themselves, but also of the acids employed in their formation, except sulphuric acid, which had been previously studied.

Before discussing any of the results which have been obtained, it will be most convenient, in the first place, to give an account of the substances employed and their magnetic rotations.

*Nitric Acid.*

A quantity of nitric acid, sp. gr. 1.52, was distilled with about 10 per cent. of  $\text{H}_2\text{SO}_4$  (100 per cent.), the first part being rejected. It was then redistilled, while a rapid current of carbonic anhydride was passed through it, according to the directions given by Kolbe (*Ann. Chem. Phys.*, **79**, 136); in this way a fraction was obtained which was very nearly colourless, b. p.  $83.7-84.7^\circ$  (corr.). The



composition of this acid was found to be 98.3 per cent. of  $\text{HNO}_3$ , or  $\text{HNO}_3 + 0.060$  mol.  $\text{OH}_2$ . The density determinations gave—

$$\begin{array}{ll} d_{4^{\circ}}^{4^{\circ}} 1.5390, & d_{15^{\circ}}^{15^{\circ}} 1.5191, \\ d_{5^{\circ}}^{5^{\circ}} 1.5368, & d_{25^{\circ}}^{25^{\circ}} 1.5043. \end{array}$$

According to Kolbe's table of densities, this acid should have a density of 1.526 at  $15^{\circ}$ . It is possible, however, that the two acids examined were not quite equally free from lower oxides of nitrogen, and this may account for this small discrepancy.

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
14°	0.5274	1.235
13	0.5303	1.240
13	0.5289	1.237
12	0.5333	1.246
12	0.5318	1.243
Average 13	0.5303	1.240
Less 0.06 mol. $\text{OH}_2$ .....		0.060
$\text{HNO}_3 =$ .....		1.180

#### *Nitric Acid and Water.*

The dilute acid was redistilled before use, nitrate of urea being added to remove lower oxides of nitrogen. Its strength was 56.74 per cent., and its composition  $\text{HNO}_3 + 2.67$  mol.  $\text{OH}_2$ .

The density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} 1.3571, \quad d_{25^{\circ}}^{25^{\circ}} 1.3474.$$

Kolbe's table gives 57 per cent. for a density of 1.358 at  $15^{\circ}$ .

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
21°	0·7987	3·646
21	0·8006	3·655
21	0·8031	3·667
Average 21	0·8008	3·656
Less OH <sub>2</sub> . . . . .		2·670
		0·986

*Methyl Nitrate.*

This was prepared from methyl alcohol, and nitric acid, nitrate of urea being added to the mixture. It boiled constantly at 65° (corr.). The density determinations gave—

$$\begin{array}{ll}
 d_{\frac{5}{5}^{\circ}}^{5^{\circ}} 1\cdot2322, & d_{\frac{15}{15}^{\circ}}^{15^{\circ}} 1\cdot2167, \\
 d_{\frac{10}{10}^{\circ}}^{10^{\circ}} 1\cdot2241, & d_{\frac{20}{20}^{\circ}}^{20^{\circ}} 1\cdot2096, \\
 & d_{\frac{25}{25}^{\circ}}^{25^{\circ}} 1\cdot2032.
 \end{array}$$

Dumas and Peligot give 1·182 at 20° (A 15, 26).

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
12·0°	0·5852	2·050
13·5	0·5887	2·066
14·0	0·5863	2·058
14·5	0·5842	2·052
5·0	0·5951	2·065
5·5	0·5930	2·059
5·8	0·5912	2·054
6·0	0·5918	2·057
Average 9·5	0·5894	2·057

*Ethyl Nitrate.*

The specimen used boiled at 87·5—87·7° (corr.). The density determinations gave—

$$\begin{array}{ll}
 d_{\frac{4}{4}^{\circ}}^{4^{\circ}} 1\cdot1305, & d_{\frac{15}{15}^{\circ}}^{15^{\circ}} 1\cdot1159, \\
 d_{\frac{10}{10}^{\circ}}^{10^{\circ}} 1\cdot1220, & d_{\frac{20}{20}^{\circ}}^{20^{\circ}} 1\cdot1099, \\
 & d_{\frac{25}{25}^{\circ}}^{25^{\circ}} 1\cdot1044.
 \end{array}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
11·0°	0·6811	3·073
9·8	0·6847	3·084
9·8	0·6862	3·091
9·5	0·6873	3·095
10·6	0·6831	3·080
10·0	0·6864	3·093
9·5	0·6828	3·075
9·0	0·6846	3·081
Average 9·9	0·6845	3·084

*Propyl Nitrate.*

This was prepared from propyl alcohol and nitric acid, nitrate of urea being previously dissolved in the acid. After fractioning a few times, it was obtained boiling at 110·2—110·7° (corr.). The boiling point given by Wallach and Schulze (B 14, 421) is 110·5°. The density determinations gave—

$$\begin{aligned}
 d_{\frac{5}{5}}^{5^{\circ}} 1\cdot0747, & \qquad d_{\frac{15}{15}}^{15^{\circ}} 1\cdot0631, \\
 d_{\frac{10}{10}}^{10^{\circ}} 1\cdot0688, & \qquad d_{\frac{20}{20}}^{20^{\circ}} 1\cdot0580, \\
 d_{\frac{25}{25}}^{25^{\circ}} 1\cdot0531.
 \end{aligned}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
10·0°	0·7483	4·085
10·0	0·7507	4·097
10·0	0·7483	4·083
9·6	0·7489	4·086
5·5	0·7536	4·093
5·5	0·7499	4·072
5·5	0·7539	4·085
5·5	0·7519	4·083
Average 7·7	0·7507	4·085

*Isobutyl Nitrate.*

This was fractioned a few times, and the portion boiling between

123.5—124.5° selected for examination. Its density determinations gave—

$$\begin{array}{ll} d_{4^{\circ}}^{4^{\circ}} 1.0334, & d_{15^{\circ}}^{15^{\circ}} 1.0215, \\ d_{10^{\circ}}^{10^{\circ}} 1.0264, & d_{20^{\circ}}^{20^{\circ}} 1.0168, \\ & d_{25^{\circ}}^{25^{\circ}} 1.0124. \end{array}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
13.5°	0.8020	5.184
10.5	0.8012	5.163
10.0	0.8035	5.175
9.8	0.8049	5.184
9.6	0.8012	5.158
9.8	0.8070	5.197
9.7	0.8049	5.183
9.6	0.8055	5.186
9.5	0.8056	5.188
6.0	0.8116	5.206
6.0	0.8093	5.190
5.6	0.8057	5.164
5.6	0.8054	5.163
Average 8.9	0.8052	5.180

### *Ethylene Nitrate. Nitroglycol.*

This was prepared in the same way as nitroglycerin, only using glycol instead of glycerin (p. 685). After being well washed with water and then with a solution of sodium carbonate, it was obtained as a pale yellow oil. This was well dried over anhydrous potassium carbonate, allowed to stand until clear, and then decanted for use. This substance was first obtained by Henry (*Ber.*, **3**, 529). As mentioned by him, it detonates when struck on an anvil, but not so easily as nitroglycerin. When heated in a test-tube, it gives off a small quantity of red fumes, boils, and distils up the side of the tube; if strongly heated it explodes with great violence.

Nitroglycol is a somewhat thick, clear, pale yellow oil; the colour is believed to be due to a small amount of impurity, as it disappears after some weeks. It requires several times its volume of alcohol for solution. Aqueous potash has but little action on it in the cold, but decomposes it on boiling, producing a brown liquid. Cold alcoholic potash does not act rapidly upon this substance at first, but the

mixture gradually becomes warm, and afterwards boils violently, becoming brown. The density determinations gave—

$$\begin{array}{ll} d_{4}^{4^{\circ}} 1.5099, & d_{15}^{15^{\circ}} 1.4960, \\ d_{10}^{10^{\circ}} 1.5012, & d_{20}^{20^{\circ}} 1.4908, \\ & d_{25}^{25^{\circ}} 1.4860. \end{array}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
13.5°	0.6657	3.753
13.5	0.6657	3.753
13.5	0.6654	3.752
13.5	0.6664	3.774
13.5	0.6709	3.774
10.6	0.6697	3.767
11.5	0.6700	3.772
11.5	0.6700	3.772
12.4	0.6735	3.795
Average 12.6	0.6686	3.768

### *Nitroglycerin.*

To prepare this, 60 c.c. of nitric acid, density 1.42, freed from any red fumes by nitrate of urea, were mixed with 100 c.c. of sulphuric acid and 20 c.c. of 45 per cent. fuming sulphuric acid; this mixture was cooled with ice, and 20 c.c. of glycerin gradually added. After standing a few hours, the product was poured into a large bulk of water, the nitroglycerin collected and washed with water, and then with a solution of sodium carbonate. A good deal of difficulty was experienced in getting the nitroglycerin sufficiently clear for examination, but it was accomplished eventually by heating it to about 30°, so as to render it more fluid, and placing it in contact with anhydrous potassium carbonate. After keeping it at this temperature, it was allowed to cool, and in about 24 hours it was warmed again and filtered through paper, a vacuum pump being used. Finally a little phosphoric anhydride was shaken with it, and after standing for some time it was decanted for use. Its density determinations gave—

$$\begin{array}{ll} d_{4}^{4^{\circ}} 1.6144, & d_{15}^{15^{\circ}} 1.6009 \\ d_{10}^{10^{\circ}} 1.6066, & d_{20}^{20^{\circ}} 1.5958, \\ & d_{25}^{25^{\circ}} 1.5910. \end{array}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
14·0°	0·6865	5·404
13·0	0·6860	5·396
12·5	0·6857	5·392
12·0	0·6875	5·404
12·0	0·6877	5·406
12·0	0·6880	5·408
14·8	0·6848	5·393
15·5	0·6897	5·428
16·0	0·6869	5·415
Average 13·5	0·6870	5·405

*Isobutyl Nitrite.*

This product was purified first by shaking with dry potassium carbonate, and fractionally distilling until the temperature rose to 77°; the distillate was then again treated with potassium carbonate and re-fractioned a few times in a Wurtz flask with a very long neck. The product collected for examination boiled at 67—68°. It was left with potassium carbonate for a short time and then decanted for use. The density determinations gave—

$$\begin{aligned}
 d_{\frac{4}{4}}^{\frac{4}{4}} & 0\cdot8878, & d_{\frac{15}{15}}^{\frac{15}{15}} & 0\cdot8752, \\
 d_{\frac{10}{10}}^{\frac{10}{10}} & 0\cdot8806, & d_{\frac{20}{20}}^{\frac{20}{20}} & 0\cdot8702, \\
 d_{\frac{25}{25}}^{\frac{25}{25}} & 0\cdot8652.
 \end{aligned}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
4·5°	0·8545	5·511
4·8	0·8533	5·506
4·8	0·8527	5·502
5·0	0·8521	5·500
13·5	0·8484	5·537
13·0	0·8428	5·497
12·0	0·8475	5·521
Average 8·2	0·8502	5·510

*Nitromethane.*

This substance was dried with potassium carbonate. When distilled, it nearly all came over at  $101^{\circ}$  (corr.). The density determinations gave—

$$\begin{array}{ll} d_{4^{\circ}}^{4^{\circ}} 1.1580, & d_{15^{\circ}}^{15^{\circ}} 1.1441, \\ d_{10^{\circ}}^{10^{\circ}} 1.1502, & d_{20^{\circ}}^{20^{\circ}} 1.1382 \\ & d_{25^{\circ}}^{25^{\circ}} 1.1330. \end{array}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
9.8°	0.6289	1.853
9.6	0.6289	1.852
9.6	0.6282	1.853
9.6	0.6304	1.857
10.7	0.6280	1.852
10.3	0.6301	1.857
10.0	0.6363	1.875
9.5	0.6325	1.862
Average 9.9	0.6304	1.858

*Nitroethane.*

The specimen used was dried with potassium carbonate. It boiled at  $114\text{--}115^{\circ}$  (corr.).

The density determinations gave—

$$\begin{array}{ll} d_{4^{\circ}}^{4^{\circ}} 1.0685, & d_{15^{\circ}}^{15^{\circ}} 1.0561, \\ d_{10^{\circ}}^{10^{\circ}} 1.0615, & d_{20^{\circ}}^{20^{\circ}} 1.0509, \\ & d_{25^{\circ}}^{25^{\circ}} 1.0461. \end{array}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
12·5°	0·7204	2·835
11·5	0·7207	2·833
10·5	0·7244	2·845
9·2	0·7257	2·848
10·5	0·7191	2·824
9·6	0·7284	2·858
9·2	0·7209	2·827
9·0	0·7203	2·824
Average 10·2	0·7224	2·837

*Nitropropane.*

This substance was prepared in the usual manner with silver nitrite and propyl iodide. These substances when mixed do not react quickly, but after a very few minutes ebullition sets in with vigour, and the silver salt fuses, apparently owing to the formation of a compound of the iodide and nitrite. It was therefore found better to add the nitrite to the iodide in small quantities at a time and to get the reaction over before adding more; in this way no fusible silver compound was formed. On distilling the product, a mixture of nitrite of propyl, nitropropane, and propyl iodide was obtained. The nitrite was roughly fractioned off and the residual oil treated with successive portions of silver nitrite until perfectly free from propyl iodide; it was then distilled and carefully fractioned a number of times. It boiled at 130·5—131·5° (corr.) and was perfectly colourless.

The density determinations gave—

$$\begin{array}{ll}
 d_{4^{\circ}}^{4^{\circ}} 1\cdot0221, & d_{15^{\circ}}^{15^{\circ}} 1\cdot0108, \\
 d_{10^{\circ}}^{10^{\circ}} 1\cdot0157, & d_{20^{\circ}}^{20^{\circ}} 1\cdot0062, \\
 & d_{25^{\circ}}^{25^{\circ}} 1\cdot0023.
 \end{array}$$

The magnetic rotations gave—



<i>t.</i>	Sp. rotation.	Mol. rotation.
20·0°	0·7781	3·824
20·0	0·7763	3·814
18·5	0·7842	3·849
18·5	0·7791	3·823
18·5	0·7763	3·809
18·5	0·7801	3·828
18·5	0·7791	3·823
20·0	0·7762	3·814
19·0	0·7776	3·827
19·0	0·7702	3·782
Average 18·9	0·7777	3·819

*Chloropicrin.*

This substance was first dried with phosphoric anhydride, and then distilled from anhydrous potassium carbonate. It boiled constantly at 112° (corr.).

The density determinations gave—

$$\begin{array}{ll}
 d_{4}^{4^{\circ}} 1\cdot6855, & d_{15^{\circ}}^{15^{\circ}} 1\cdot6670, \\
 d_{10^{\circ}}^{10^{\circ}} 1\cdot6748, & d_{20^{\circ}}^{20^{\circ}} 1\cdot6594, \\
 d_{25^{\circ}}^{25^{\circ}} 1\cdot6528.
 \end{array}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
15·6°	0·9800	5·376
15·6	0·9804	5·378
15·6	0·9800	5·376
15·6	0·9775	5·363
15·6	0·9810	5·382
9·0	0·9905	5·399
9·0	0·9887	5·389
9·0	0·9905	5·399
9·0	0·9899	5·395
Average 12·7	0·9843	5·384

*Ammonia.**a. Aqueous Solution.*

The product employed contained 31 per cent. of  $\text{NH}_3$ , and therefore had the composition  $\text{NH}_3 + 2\cdot10 \text{ mol. OH}_2$ .

The density determinations gave—

$$d_{4^{\circ}}^{4^{\circ}} 0.8989, \quad d_{10^{\circ}}^{10^{\circ}} 0.8955,$$

$$d_{15^{\circ}}^{15^{\circ}} 0.8926.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
9.5°	1.1523	3.916
9.5	1.1491	3.905
9.5	1.1489	3.904
9.5	1.1516	3.913
9.5	1.1499	3.908
10.0	1.1518	3.916
9.5	1.1527	3.917
9.5	1.1506	3.910
9.5	1.1473	3.899
Average 9.5	1.1505	3.910
Less OH <sub>2</sub> , 2.10 mol. ....		2.100
NH <sub>3</sub> .....		1.810

*b. Alcoholic Solution.*

This was prepared with absolute alcohol that had been standing over anhydrous copper sulphate for months. It was then decanted and distilled. The solution contained 14.48 per cent. of NH<sub>3</sub>, and therefore had the composition NH<sub>3</sub> + 2.18 mol. C<sub>2</sub>H<sub>6</sub>O. It was saturated as far as would permit of its use with safety, and began to give off gas at about 15°.

The density determinations gave—

$$d_{4^{\circ}}^{4^{\circ}} 0.7829, \quad d_{8^{\circ}}^{8^{\circ}} 0.7794.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
9°	0.9404	7.872
9	0.9385	7.858
9	0.9459	7.920
9	0.9417	7.885
9	0.9429	7.895
Average 9	0.9419	7.886
Less 2.18 mol. C <sub>2</sub> H <sub>6</sub> O .....		6.060
NH <sub>3</sub> = .....		1.826

*Ethylamine.*

This and most of the other compound ammonias examined were obtained from Kahlbaum.

The product used was kept over freshly fused caustic potash some days before distillation. When fractioned, it mostly came over between 17·4 and 18·4°, and the specimen examined had this boiling point. The density determinations gave—

$$d_{4^{\circ}}^{4^{\circ}} 0\cdot7013, \quad d_{10^{\circ}}^{10^{\circ}} 0\cdot6946,$$

$$d_{15^{\circ}}^{15^{\circ}} 0\cdot6892.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
4·5°	1·0068	3·592
4·5	1·0048	3·585
4·5	1·0103	3·605
4·5	1·0106	3·606
5·0	1·0106	3·608
5·0	1·0130	3·617
5·0	1·0180	3·631
4·5	1·0122	3·611
5·0	1·0098	3·605
5·2	1·0125	3·616
5·4	1·0140	3·623
5·4	1·0116	3·614
8·6	1·0054	3·610
8·3	1·0023	3·598
8·6	1·0067	3·615
9·3	1·0057	3·610
Average 5·8	1·0097	3·609

*Diethylamine.*

This was carefully fractioned several times; the bulk of the product then boiled at 56—57° (corr.), which appears to be about the true boiling point of this base. The density determinations gave—

$$d_{4^{\circ}}^{4^{\circ}} 0\cdot7226, \quad d_{15^{\circ}}^{15^{\circ}} 0\cdot7116,$$

$$d_{10^{\circ}}^{10^{\circ}} 0\cdot7164, \quad d_{20^{\circ}}^{20^{\circ}} 0\cdot7070,$$

$$d_{25^{\circ}}^{25^{\circ}} 0\cdot7028.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
5.4°	1.0095	5.682
5.4	1.0054	5.658
5.4	1.0033	5.647
5.4	1.0060	5.662
13.5	0.9952	5.662
14.0	0.9923	5.649
14.5	0.9960	5.674
Average 9.1	1.0011	5.662

*Triethylamine.*

The specimen employed contained a little diethylamine; it was therefore fractioned several times from sodium, which forms a compound with this base. The portion selected for examination boiled at 89—89.5° (corr.), mostly at 89°. The density determinations gave—

$$\begin{aligned}
 d_{4^{\circ}}^{4^{\circ}} & 0.7426, & d_{15^{\circ}}^{15^{\circ}} & 0.7331, \\
 d_{10^{\circ}}^{10^{\circ}} & 0.7372, & d_{20^{\circ}}^{20^{\circ}} & 0.7294, \\
 d_{25^{\circ}}^{25^{\circ}} & 0.7257.
 \end{aligned}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
10.4°	1.1151	8.496
10.3	1.1157	8.499
10.3	1.1169	8.508
10.3	1.1189	8.523
10.0	1.1203	8.532
9.8	1.1194	8.522
9.6	1.1192	8.518
9.3	1.1233	8.547
Average 10.0	1.1186	8.518

*Propylamine.*

The specimen examined boiled at 47.5—48.5° (corr.). The density determinations gave—

$$\begin{aligned}
 d_{4^{\circ}}^{4^{\circ}} & 0.7330, & d_{15^{\circ}}^{15^{\circ}} & 0.7222, \\
 d_{10^{\circ}}^{10^{\circ}} & 0.7268, & d_{20^{\circ}}^{20^{\circ}} & 0.7182, \\
 & & d_{25^{\circ}}^{25^{\circ}} & 0.7144.
 \end{aligned}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
6.5°	1.0116	4.540
5.5	1.0161	4.554
5.0	1.0190	4.563
5.0	1.0176	4.557
5.0	1.0183	4.560
15.0	1.0134	4.597
14.5	1.0094	4.579
15.0	1.0064	4.568
15.5	1.0050	4.563
Average 9.6	1.0130	4.564

*Dipropylamine.*

After being distilled two or three times, most of the product was obtained boiling between 109.4° and 110.4°. The density determinations gave—

$$\begin{aligned}
 d_{4^{\circ}}^{4^{\circ}} & 0.7524, & d_{15^{\circ}}^{15^{\circ}} & 0.7430, \\
 d_{10^{\circ}}^{10^{\circ}} & 0.7471, & d_{20^{\circ}}^{20^{\circ}} & 0.7393, \\
 & & d_{25^{\circ}}^{25^{\circ}} & 0.7357.
 \end{aligned}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
5.8	1.0087	7.539
5.8	1.0051	7.512
5.8	1.0101	7.550
6.5	1.0122	7.571
6.5	1.0101	7.556
15.0	1.0000	7.553
16.2	0.9975	7.558
16.8	0.9960	7.553
17.5	0.9968	7.547
Average 10.7	1.0041	7.549

*Tripropylamine.*

To obtain this, dipropylamine, alcohol, and propyl iodide in equal volumes were heated in a sealed tube at  $100^{\circ}$  for two or three hours. On cooling, the product solidified to a crystalline mass. After distilling with water to remove alcohol and propyl iodide, potash was added, and the volatile bases distilled off; these when dried and fractionated gave tripropylamine boiling at  $155.5$ — $156.5^{\circ}$ . This was again distilled after boiling with sodium for some time, which attacks any dipropylamine present. The boiling point, however, was not changed by this treatment. The iodide of tetrapropylammonium which was left after the removal of the volatile bases was distilled, the mixture of propyl iodide and tripropylamine thus obtained treated with hydrochloric acid, &c. The tripropylamine obtained in this way boiled at  $155$ — $157^{\circ}$ , but mostly at  $156^{\circ}$ , which is apparently the boiling point of this base. Römer gives it as  $144$ — $146^{\circ}$  (*Ber.*, **6**, 1101).

The density determinations gave—

$$\begin{array}{ll} d_{4^{\circ}}^{4^{\circ}} 0.7681, & d_{15^{\circ}}^{15^{\circ}} 0.7600, \\ d_{10^{\circ}}^{10^{\circ}} 0.7634, & d_{20^{\circ}}^{20^{\circ}} 0.7567, \\ & d_{25^{\circ}}^{25^{\circ}} 0.7539. \end{array}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
10.9	1.1167	11.631
9.7	1.1238	11.691
9.0	1.1252	11.699
9.2	1.1247	11.696
10.3	1.1205	11.666
10.3	1.1152	11.610
10.3	1.1208	11.669
10.3	1.1194	11.654
Average 10.0	1.1208	11.664

*Isobutylamine.*

The base employed boiled between about  $67^{\circ}$  and  $74^{\circ}$ . On repeatedly fractionating, the chief part was found to come over at  $68$ — $69^{\circ}$  (corr.). Hughes and Römer (*Ber.*, **7**, 511) give it as  $65.5^{\circ}$ ; this is believed to be too low.

Its density determinations gave—

$$\begin{aligned} d_{4^{\circ}}^{4^{\circ}} & 0.7464, & d_{15^{\circ}}^{15^{\circ}} & 0.7363, \\ d_{10^{\circ}}^{10^{\circ}} & 0.7408, & d_{20^{\circ}}^{20^{\circ}} & 0.7322, \\ & & d_{25^{\circ}}^{25^{\circ}} & 0.7283. \end{aligned}$$

The magnetic rotations gave—

<i>t</i> .	Sp. rotation.	Mol. rotation.
17.8	1.0320	5.699
16.2	1.0355	5.711
15.0	1.0344	5.697
15.0	1.0341	5.696
15.0	1.0350	5.704
15.5	1.0313	5.684
14.5	1.0313	5.694
14.5	1.0284	5.661
14.5	1.0328	5.684
Average 15.3	1.0331	5.692

#### *Isobutylamine and Water.*

Isobutylamine, when mixed with water, develops heat. The mixture examined consisted of equal vols. at 15° of each substance; the density of the mixture was for  $d_{15^{\circ}}^{15^{\circ}}$  0.9002; this shows that considerable condensation occurs on making this mixture, the average density of equal vols. of isobutylamine and water being as follows:—

$$\begin{array}{rcl} \text{Isobutylamine } d_{15^{\circ}}^{15^{\circ}} & 0.7362 & \\ \text{Water.....} & 1.0000 & \\ \hline \text{Average density .} & 0.8681 & \end{array}$$

The molecular composition of this mixture is  $C_4H_{11}N + 5.51OH_2$ .  
The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
15°	1·0460	11·091
15	1·0484	11·116
15	1·0402	11·030
15	1·0431	11·060
15	1·0460	11·091
Average 15	1·0447	11·077
Less OH <sub>2</sub> .....		5·510
		5·567

*Isobutylamine and Alcohol.*

These substances were mixed in equal volumes measured at 15°. The composition of the mixture is represented by C<sub>4</sub>H<sub>11</sub>N + 1·715 mol. C<sub>2</sub>H<sub>6</sub>O.

The density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} 0\cdot791.$$

The average density of equal volumes of isobutylamine and alcohol at 15° is—

Alcohol (spec. used) .....	0·7948
Isobutylamine .....	0·7357
Average .....	0·7652

This shows that considerable contraction takes place on mixing these substances.

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
15°	0·9556	10·364
15	0·9541	10·348
15	0·9556	10·364
15	0·9548	10·356
15	0·9655	10·418
15	0·9587	10·342
15	0·9620	10·377
15	0·9596	10·351
15	0·9572	10·326
Average 15	0·9581	10·361
Less alcohol .....		4·768
		5·593



*Diisobutylamine.*

This product, after several fractional distillations, was obtained with a boiling point of 139—140° (corr.). Merz and Gasiorowski (*Ber.*, **17**, 626) give it as 135—137°. The original substance was very good, very little high and low portions being separated by distillation.

The density determinations gave—

$$\begin{array}{ll} d_{\frac{4}{4}}^{4^{\circ}} 0.7577, & d_{15}^{15^{\circ}} 0.7491, \\ d_{10}^{10^{\circ}} 0.7528, & d_{20}^{20^{\circ}} 0.7457, \\ & d_{25}^{25^{\circ}} 0.7425. \end{array}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
16.3	1.0409	9.969
15.3	1.0442	9.992
15.0	1.0412	9.961
15.0	1.0385	9.935
16.0	1.0373	9.933
15.5	1.0334	9.891
15.0	1.0382	9.932
14.5	1.0373	9.918
14.5	1.0378	9.924
14.5	1.0349	9.895
14.5	1.0401	9.945
Average 15.1	1.0385	9.936

*Allylamine.*

The specimen used came over mostly at 53.2—54°. It was fractioned several times, and the specimen selected boiled at 53.2—53.4 (corr.). The boiling point given by Rinne is 58° (*Annalen*, 168—262). When smelt, it causes sneezing.

The density determinations gave—

$$\begin{array}{ll} d_{\frac{4}{4}}^{4^{\circ}} 0.7799, & d_{15}^{15^{\circ}} 0.7688, \\ d_{10}^{10^{\circ}} 0.7739, & d_{20}^{20^{\circ}} 0.7436, \\ & d_{25}^{25^{\circ}} 0.7583. \end{array} \quad *$$

Rinne gives the density as 0·864 at 15°.

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
13·5°	1·3605	5·593
13·0	1·3642	5·609
13·0	1·3615	5·598
13·0	1·3620	5·599
15·5	1·3520	5·572
15·5	1·3508	5·567
15·5	1·3545	5·583
15·5	1·3548	5·584
Average 14·3	1·3575	5·588

*Pentamethylenediamine*,  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$ .

The product examined was prepared by my son (W. H. P.). It boiled at 178—179° (corr.). Its density determinations gave—

$$\begin{aligned}
 d_{\frac{4}{4}}^{\frac{4}{4}} & 0\cdot8939, & d_{\frac{15}{15}}^{\frac{15}{15}} & 0\cdot8855, \\
 d_{\frac{10}{10}}^{\frac{10}{10}} & 0\cdot8890, & d_{\frac{20}{20}}^{\frac{20}{20}} & 0\cdot8822, \\
 d_{\frac{25}{25}}^{\frac{25}{25}} & 0\cdot8792.
 \end{aligned}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
13°	1·1719	7·488
13	1·1697	7·473
13	1·1731	7·495
13	1·1709	7·481
13	1·1768	7·519
Average 13	1·1725	7·491

As I had some quantity of this substance at my disposal, and it readily absorbs moisture, it was carefully fractioned. The chief part of the product boiled at 178—180·5° (corr.) (a little of that which came over first, and which probably contained a small quantity of water, being collected separately). The density determinations gave—

$$\begin{aligned}
 d_{+}^{4^{\circ}} 0.8930, & \quad d_{15^{\circ}}^{15^{\circ}} 0.8846, \\
 d_{10^{\circ}}^{10^{\circ}} 0.8881, & \quad d_{20^{\circ}}^{20^{\circ}} 0.8812, \\
 d_{25^{\circ}}^{25^{\circ}} 0.8784.
 \end{aligned}$$

Ladenburgh gives its boiling point as  $175-178^{\circ}$ , and its density at  $d_{+}^{(0)}$  as 0.9174 (*Ber.*, **18**, 2957).

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
11.7	1.1703	7.496
11.7	1.1673	7.477
14.7	1.1713	7.503
14.7	1.1703	7.496
Average 11.7	1.1698	7.493

This refracted product, therefore, has given numbers for the molecular rotation practically identical with those obtained with the original product, a small difference being observable in the specific rotation, which is a little lower. The influence of this is neutralised by the slight change in the density. The average molecular rotation is 7.492.

### *Piperidine.*

The specimen of this base used in the investigation boiled at  $105.8-106.3$  (corr.). The density determinations gave—

$$\begin{aligned}
 d_{+}^{4^{\circ}} 0.8758, & \quad d_{15^{\circ}}^{15^{\circ}} 0.8664, \\
 d_{10^{\circ}}^{10^{\circ}} 0.8704, & \quad d_{20^{\circ}}^{20^{\circ}} 0.8626, \\
 d_{25^{\circ}}^{25^{\circ}} 0.8591.
 \end{aligned}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
11.0	1.0714	5.826
11.3	1.0676	5.806
11.3	1.0684	5.811
11.0	1.0670	5.803
16.0	1.0641	5.805
14.5	1.0686	5.821
14.5	1.0659	5.803
14.0	1.0665	5.807
Average 13.0	1.0674	5.810

*Piperidine and Water.*

This base has a great attraction for water. The proportions used were molecular,  $C_5H_{11}N + OH_2$ . The density determinations gave—

$$\begin{aligned}
 d_{\frac{4}{4}}^{\frac{4}{4}} & 0.9227, & d_{15^{\circ}}^{15^{\circ}} & 0.9133, \\
 d_{10^{\circ}}^{10^{\circ}} & 0.9173, & d_{20^{\circ}}^{20^{\circ}} & 0.9097, \\
 & & d_{25^{\circ}}^{25^{\circ}} & 0.9063.
 \end{aligned}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
16.0	1.0724	6.724
15.2	1.0709	6.711
15.3	1.0727	6.722
14.5	1.0783	6.753
16.0	1.0696	6.707
16.0	1.0732	6.729
Average 15.5	1.0728	6.724 1.000
		5.724

*Pyridine.*

The specimen used was obtained from Schuchardt. When kept with freshly-fused potassium hydrate, it did not show any signs of containing water; after several fractional distillations, the principal part of the product was obtained boiling between  $116.2-116.7^{\circ}$  (corr.). The density determinations gave—

$$\begin{aligned}
 d_{\frac{4}{4}^{\circ}}^{4^{\circ}} & 0.9944, & d_{\frac{15}{15}^{\circ}}^{15^{\circ}} & 0.9855, \\
 d_{\frac{10}{10}^{\circ}}^{10^{\circ}} & 0.9894, & d_{\frac{20}{20}^{\circ}}^{20^{\circ}} & 0.9816, \\
 d_{\frac{25}{25}^{\circ}}^{25^{\circ}} & 0.9778.
 \end{aligned}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
10.5	1.9734	8.758
10.8	1.9686	8.738
10.8	1.9731	8.758
10.8	1.9740	8.762
10.8	1.9682	8.736
14.5	1.9741	8.789
14.3	1.9724	8.777
13.0	1.9723	8.770
Average 12.0	1.9720	8.761

*Propionitrile.*

This was well dried with anhydrous potassium carbonate and then carefully fractioned. The specimen examined boiled at 98—98.5° (corr.). The density determinations gave—

$$\begin{aligned}
 d_{\frac{4}{4}^{\circ}}^{4^{\circ}} & 0.7998, & d_{\frac{16}{15}^{\circ}}^{16^{\circ}} & 0.7896, \\
 d_{\frac{15}{10}^{\circ}}^{15^{\circ}} & 0.7941, & d_{\frac{20}{20}^{\circ}}^{20^{\circ}} & 0.7853, \\
 d_{\frac{25}{25}^{\circ}}^{25^{\circ}} & 0.7815.
 \end{aligned}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
10.5	0.8641	3.327
10.5	0.8662	3.335
11.0	0.8668	3.339
11.5	0.8624	3.324
12.0	0.8612	3.322
16.0	0.8624	3.341
16.3	0.8588	3.328
16.7	0.8587	3.329
Average 13.06	0.8626	3.331

*Trimethylene Cyanide.*

Obtained by digesting trimethylene bromide with cyanide of potassium and alcohol. The portion examined boiled at 285—287·4° (corr.). Henry gives it as 274° (*Bull. Chem. Soc.*, **43**, 618). The density determinations gave—

$$\begin{aligned} d_{4^{\circ}}^{4^{\circ}} & 1\cdot0031, & d_{15^{\circ}}^{15^{\circ}} & 0\cdot9952, \\ d_{10^{\circ}}^{10^{\circ}} & 0\cdot9984, & d_{20^{\circ}}^{20^{\circ}} & 0\cdot9922, \\ & & d_{25^{\circ}}^{25^{\circ}} & 0\cdot9894. \end{aligned}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
10·0	0·9850	5·152
10·5	0·9841	5·149
11·0	0·9856	5·160
10·5	0·9801	5·128
10·5	0·9786	5·120
10·5	0·9786	5·120
10·5	0·9792	5·123
Average 10·5	0·9816	5·136

*Hydrochloric Acid.*

The strength of the acids examined was determined by titration, and also by precipitation.

*Solution I.*—Saturated at about 20°. It contained 41·70 per cent. of HCl; its composition was, therefore, HCl + 2·834 mol. OH<sub>2</sub>.

The density determinations gave—

$$\begin{aligned} d_{4^{\circ}}^{4^{\circ}} & 1\cdot2154, & d_{10^{\circ}}^{10^{\circ}} & 1\cdot2113, \\ & & d_{15^{\circ}}^{15^{\circ}} & 1\cdot2082. \end{aligned}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
16.5°	1.7130	6.882
16.5	1.7115	6.876
16.5	1.7123	6.863
16.5	1.7113	6.875
16.5	1.7112	6.887
19.8	1.7110	6.884
19.7	1.7113	6.885
Average 17.3	1.7117	6.879
Less OH <sub>2</sub> .....		2.834
		4.045

*Solution II.*—This contained 36.5 per cent. of HCl. The composition was therefore HCl + 3.51 mol. OH<sub>2</sub>.

The density determinations gave—

$$d_{4^{\circ}}^{4^{\circ}} 1.1939, \quad d_{15^{\circ}}^{15^{\circ}} 1.1866,$$

$$d_{25^{\circ}}^{25^{\circ}} 1.1827.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
11.6°	1.6575	7.724
11.5	1.6590	7.731
11.5	1.6581	7.727
11.5	1.6569	7.721
11.5	1.6557	7.716
10.3	1.6613	7.737
10.3	1.6580	7.722
10.3	1.6599	7.731
10.3	1.6580	7.722
Average 11.0	1.6583	7.725
Less 3.351 mol. OH <sub>2</sub> .....		3.510
HCl = .....		4.215

*Solution III.*—This contained 30.86 per cent. of HCl; its composition was, therefore, HCl + 4.543 mol. OH<sub>2</sub>.

The density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} 1.1582, \quad d_{25^{\circ}}^{25^{\circ}} 1.1548.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
21.5°	1.5554	8.841
21.5	1.5528	8.826
21.5	1.5577	8.854
21.5	1.5580	8.856
21.5	1.5572	8.852
Average 21.5	1.5562	8.846
Less OH <sub>2</sub> .....		4.543
		4.303

*Solution IV.*—This contained 25.6 per cent. of HCl; its composition was, therefore, HCl + 5.893 mol. OH<sub>2</sub>.

The density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} 1.1288, \quad d_{25^{\circ}}^{25^{\circ}} 1.1260.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
21.0	1.4684	10.319
21.0	1.4706	10.334
21.0	1.4643	10.290
21.0	1.4669	10.306
20.0	1.4606	10.261
20.0	1.4643	10.289
20.0	1.4599	10.257
20.0	1.4643	10.288
20.0	1.4721	10.343
Average 20.4	1.4657	10.298
Less OH <sub>2</sub> .....		5.893
		4.405

*Solution V.*—This contained 15.63 per cent. of HCl; its composition was, therefore, HCl + 10.856 mol. OH<sub>2</sub>.

The density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} 1.0771, \quad d_{25^{\circ}}^{25^{\circ}} 1.0745.$$

The magnetic rotations gave—



<i>t.</i>	Sp. rotation.	Mol. rotation.
16°	1·2748	15·254
16	1·2790	15·303
16	1·2761	15·268
Average 16	1·2766	15·275
Less OH <sub>2</sub> .....		10·856
		4·419

*Hydrochloric Acid in Isomyl Oxide.*

This contained 10·68 per cent. HCl; its composition was, therefore, HCl + 1·932 mol. C<sub>10</sub>H<sub>22</sub>O. The density determinations gave—

$$d_{4^{\circ}}^{4^{\circ}} 0\cdot8252, \quad d_{15}^{15^{\circ}} 0\cdot8159,$$

$$d_{25}^{25^{\circ}} 0\cdot8132.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
20·0°	1·0223	23·834
19·5	1·0169	23·693
19·5	1·0223	23·834
19·5	1·0178	23·715
19·5	1·0231	23·839
Average 19·6	1·0205	23·783
Less C <sub>10</sub> H <sub>22</sub> O, 11·168 × 1·932..		21·572
		2·211

The above solution was cloudy on account of the absorption of a small quantity of water, and this rendered it difficult to read as the light was obstructed. A second solution was therefore prepared, great care being used to prevent the presence of moisture. It was obtained quite clear, and contained 12·82 per cent. of hydrochloric acid, the composition being HCl + 1·579 mol. C<sub>10</sub>H<sub>22</sub>O.

Its density determinations gave—

$$d_{10}^{10^{\circ}} 0\cdot8265, \quad d_{15}^{15^{\circ}} 0\cdot8221.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
14	1·0338	19·754
14	1·0382	19·838
14	1·0352	19·782
14	1·0352	19·782
14	1·0382	19·838
Average 14	1·0361	19·799
Less C <sub>19</sub> H <sub>20</sub> O	11·168 × 1·570 ...	17·534
		2·265
Previous No. ....		2·211
Average.....		2·238

### *Hydrobromic Acid.*

This was prepared by acting on amorphous phosphorus with bromine in the presence of water; the gas was freed from bromine vapour by twice washing it with a saturated solution of hydrobromic acid holding amorphous phosphorus in suspension.

*Solution I*, fully saturated at about 20°, contained 65·59 per cent. of HBr; its composition was, therefore, HBr + 2·361 mol. OH<sub>2</sub>. The density determinations gave—

$$d_{4^{\circ}}^{1^{\circ}} 1\cdot7978, \quad d_{10^{\circ}}^{10^{\circ}} 1\cdot7919,$$

$$d_{15^{\circ}}^{15^{\circ}} 1\cdot7874.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
16·5°	2·6154	10·047
16·5	2·6134	10·039
16·5	2·6123	10·036
16·5	2·6119	10·033
16·5	2·6093	10·023
19·5	2·6017	10·006
19·5	2·6058	10·022
Average 17·4	2·6100	10·030
Less OH <sub>2</sub> .....		2·361
		7·669

*Solution II*.—This contained 56 per cent. HBr; its composition

was, therefore,  $\text{HBr} + 3.533 \text{ mol. OH}_2$ . The density determinations gave—

$$d_{15^\circ}^{15^\circ} 1.6117, \quad d_{25}^{25^\circ} 1.6064.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation	Mol. rotation.
22°	2.3213	11.597
22	2.3206	11.594
22	2.3202	11.591
22	2.3199	11.590
22	2.3213	11.597
Average 22	2.3207	11.594
Less $\text{OH}_2$ .....		3.533
		8.061

*Solution III.*—This contained 39.71 per cent.  $\text{HBr}$ : its composition was, therefore,  $\text{HBr} + 6.831 \text{ mol. OH}_2$ . The density determinations gave—

$$d_{4^\circ}^{4^\circ} 1.3850, \quad d_{15^\circ}^{15^\circ} 1.3786,$$

$$d_{25}^{35^\circ} 1.3748.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
22.3°	1.8482	15.224
22.3	1.8436	15.186
21.0	1.8498	15.247
21.0	1.8462	15.224
21.0	1.8523	15.273
21.0	1.8534	15.276
20.0	1.8510	15.242
20.0	1.8539	15.266
20.0	1.8549	15.275
Average 21.0	1.8503	15.246
Less $\text{OH}_2$ .....		6.831
		8.415

*Solution IV.*—This contained 24.6 per cent. of  $\text{HBr}$ ; its composition was, therefore,  $\text{HBr} + 13.789 \text{ mol. OH}_2$ . The density determinations gave—

$$d_{\frac{15^\circ}{15^\circ}}^{15^\circ} 1.2049,$$

$$d_{\frac{25^\circ}{25^\circ}}^{25^\circ} 1.2028.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
18°	1.4684	22.261
18	1.4728	22.367
18	1.4721	22.356
18	1.4716	22.349
18	1.4718	22.351
Average 18	1.4713	22.336
Less OH <sub>2</sub> .....		13.789
		8.547

*Solution V.*—This contained 15.47 per cent. of HBr; its composition was, therefore, HBr + 24.580 mol. OH<sub>2</sub>. The density determinations gave—

$$d_{\frac{15^\circ}{15^\circ}}^{15^\circ} 1.1172,$$

$$d_{\frac{25^\circ}{25^\circ}}^{25^\circ} 1.1149.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
16.5	1.2687	33.036
16.5	1.2716	33.112
16.5	1.2731	33.151
Average 16.5	1.2711	33.099
Less OH <sub>2</sub> .....		24.580
		8.519

#### *Hydriodic Acid.*

*Solution I.*—This contained 67.02 per cent. HI; its composition was, therefore, HI + 3.498 mol. OH<sub>2</sub>. This acid was freshly prepared, colourless, and pure.

The density determinations gave—

$$d_{\frac{4^\circ}{4^\circ}}^{4^\circ} 1.9600,$$

$$d_{\frac{15^\circ}{15^\circ}}^{15^\circ} 1.9489,$$

$$d_{\frac{16^\circ}{16^\circ}}^{16^\circ} 1.9537,$$

$$d_{\frac{20^\circ}{20^\circ}}^{20^\circ} 1.9448,$$

$$d_{\frac{25^\circ}{25^\circ}}^{25^\circ} 1.9414.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
22.5°	3.9033	21.242
22.0	3.8974	21.286
20.0	3.8949	21.248
20.0	3.9027	21.291
Average 21.1	3.8996	21.267
Less OH <sub>2</sub> .....		3.498
		17.769

*Solution II.*—This contained 65.1 per cent. HI; its composition was, therefore, HI + 3.827 mol. OH<sub>2</sub>.

The density determinations gave—

$$\begin{aligned}
 d_{4^{\circ}}^{4^{\circ}} & 1.9182, & d_{15^{\circ}}^{15^{\circ}} & 1.9073, \\
 d_{10^{\circ}}^{10^{\circ}} & 1.9118, & d_{20^{\circ}}^{20^{\circ}} & 1.9035, \\
 & & d_{25^{\circ}}^{25^{\circ}} & 1.9003.
 \end{aligned}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
16.0°	3.7713	21.640
16.0	3.7833	21.709
17.0	3.7802	21.712
17.0	3.7791	21.705
16.5	3.7827	21.710
Average 16.5	3.7793	21.695
Less OH <sub>2</sub> .....		3.827
		17.868

*Solution III.*—This contained 61.97 per cent. HI; its composition was, therefore, HI + 4.364 mol. OH<sub>2</sub>.

The density determinations gave—

$$\begin{aligned}
 d_{4^{\circ}}^{4^{\circ}} & 1.8349, & d_{15^{\circ}}^{15^{\circ}} & 1.8244, \\
 d_{10^{\circ}}^{10^{\circ}} & 1.8280, & d_{20^{\circ}}^{20^{\circ}} & 1.8220.
 \end{aligned}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
18·0°	3·5713	22·483
17·5	3·5768	22·514
17·5	3·5713	22·479
17·5	3·5681	22·459
17·5	3·5705	22·474
Average 17·6	3·5716	22·481
Less OH <sub>2</sub> .....		4·364
		18·117

*Solution IV.*—Freshly distilled, colourless, and pure; it contained 56·78 per cent. HI; its composition was, therefore, HI + 5·413 mol. OH<sub>2</sub>.

The density determinations gave—

$$\begin{aligned}
 d_{\frac{4}{4}}^{4^{\circ}} & 1\cdot7115, & d_{\frac{15}{15}}^{15^{\circ}} & 1\cdot7021, \\
 d_{\frac{10}{10}}^{10^{\circ}} & 1\cdot7059, & d_{\frac{20}{20}}^{20^{\circ}} & 1\cdot6988, \\
 d_{\frac{25}{25}}^{25^{\circ}} & 1\cdot6962.
 \end{aligned}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
22·0°	3·2108	23·688
21·0	3·2166	23·723
21·0	3·2169	23·725
22·0	3·2220	23·764
21·0	3·2134	23·700
21·5	3·2171	23·731
22·0	3·2137	23·710
22·0	3·2203	23·759
22·0	3·2220	23·764
21·0	3·2166	23·723
21·5	3·2171	23·731
Average 21·5	3·2170	23·721
Less OH <sub>2</sub> .....		5·413
		18·308

*Solution V.*—This contained 42·7 per cent.; its composition was, therefore, HI + 9·542 mol. OH<sub>2</sub>.

The density determinations gave—

$$\begin{array}{ll} d_{10}^{10^\circ} 1.4536, & d_{20}^{20^\circ} 1.4484, \\ d_{15}^{15^\circ} 1.4507, & d_{25}^{25^\circ} 1.4467. \end{array}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
15.0°	2.4354	27.958
14.5	2.4367	27.989
14.5	2.4350	27.947
14.0	2.4340	27.930
17.0	2.4326	27.915
16.0	2.4385	28.003
15.5	2.4327	27.930
Average 15.2	2.4350	27.915
Less OH <sub>2</sub> .....		9.542
		18.403

*Solution VI.*—This contained 31.77 per cent.; its composition was, therefore, HI + 15.272 mol. OH<sub>2</sub>.

The density determinations gave—

$$d_{15}^{15^\circ} 1.2977, \quad d_{20}^{20^\circ} 1.2962.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
17.0°	1.9544	33.763
15.5	1.9515	33.702
15.5	1.9500	33.676
15.5	1.9544	33.752
Average 15.9	1.9526	33.723
Less OH <sub>2</sub> .....		15.272
		18.451

*Solution VII.*—This contained 20.77 per cent.; its composition was, therefore, HI + 27.128 mol. OH<sub>2</sub>.

The density determinations gave—

$$d_{15}^{15^\circ} 1.1770, \quad d_{25}^{25^\circ} 1.1754.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
23·0°	1·5636	45·539
21·0	1·5673	45·631
20·5	1·5644	45·544
20·0	1·5644	45·510
20·0	1·5649	45·554
20·0	1·5649	45·554
19·5	1·5653	45·562
19·5	1·5642	45·523
Average 20·4	1·5650	45·556
Less OH <sub>2</sub> .....		27·128
		18·428

*Ammonium Chloride.*

The specimen of this salt used was recrystallised several times and then dried over sulphuric acid in a vacuum.

The solution used contained 27·08 per cent. of salt, and therefore had the composition NH<sub>4</sub>Cl + 8OH<sub>2</sub> as nearly as possible. This solution was a supersaturated one, and although its tendency to crystallise was very inconvenient, especially in determining the density, it was thought better to put up with that than work with a weaker solution.

The density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} 1\cdot0787, \quad d_{20^{\circ}}^{20^{\circ}} 1\cdot0783,$$

$$d_{25^{\circ}}^{25^{\circ}} 1\cdot0777.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
25·0°	1·3851	14·108
22·0	1·3861	14·108
22·0	1·3846	14·090
21·0	1·3842	14·089
20·0	1·3832	14·076
20·0	1·3865	14·109
20·0	1·3850	14·095
20·0	1·3850	14·095
Average 21·2	1·3850	14·096
Less 8 mol. OH <sub>2</sub> .....		8·000
NH <sub>4</sub> Cl = .....		6·096



Attempts were made to determine the molecular weight of this substance by Raoult's process with acetic acid, but it was found to be insufficiently soluble in acetic acid.

*Ethylamine Hydrochloride.*

A nearly saturated solution of this salt was made and its strength found by determining the chlorine several times. It contained 60.58 per cent. of  $\text{EtH}_2\text{N.HCl}$ , and therefore had the composition  $\text{EtH}_2\text{N.HCl} + 2.946 \text{ mol. OH}_2$ .

The density determinations gave—

$$d_{10}^{10^\circ} 1.0535, \quad d_{20}^{20^\circ} 1.0505.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
17.0°	1.5439	10.966
17.0	1.5401	10.939
16.0	1.5393	10.929
16.0	1.5401	10.934
15.8	1.5350	10.989
15.8	1.5381	10.920
15.7	1.5401	10.934
15.7	1.5401	10.934
Average 16.1	1.5396	10.943
Less 2.946 mol. $\text{OH}_2$ .. . . .		2.946
		7.997

A determination of the molecular weight of this substance by Raoult's process in glacial acetic acid gave 115.1. Theory requires 81.5. This is high; the solution, however, was rather strong, 1.307 of salt in 100 of acid: this may have had a little to do with this result, but probably dissociation was the chief cause.

*Diethylamine Hydrochloride.*

A very nearly saturated solution of this salt was prepared. Chlorine determinations showed that it contained 61.58 per cent. The solution therefore had the composition  $\text{Et}_2\text{HN.HCl} + 3.79 \text{ mol. OH}_2$ .

The density determinations gave—

$$d_{10}^{10^\circ} 1.0198, \quad d_{20}^{20^\circ} 1.0164.$$

The magnetic rotations gave—

<i>t</i> .	Sp. rotation.	Mol. rotation.
15°	1·4113	13·694
15	1·4125	13·705
15	1·4125	13·705
15	1·4116	13·697
15	1·4100	13·682
15	1·4063	13·646
15	1·4085	13·667
15	1·4071	13·694
Average 15	1·4100	13·686
Less 3·97 mol. OH <sub>2</sub> .....		3·790
		9·896

A determination of the molecular weight of this salt by Raoult's process with acetic acid gave 139·9. Theory requires 109·5. This as in the case of the ethylamine salt is high. The proportions used were 1·072 of salt to 100 of acid.

*Solution of Diethylamine Hydrochloride in Absolute Alcohol.*

The salt used, which was dried by fusion and heated until it boiled, was dissolved while hot in alcohol of  $d_{15}^{15^{\circ}}$  0·7947. The solution was very nearly saturated at the ordinary temperature. The strength was known from the amount of salt used, and afterwards checked by chlorine estimations. The solution contained 22·63 per cent. of salt, and had the composition (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>HN, HCl + 8·138 mol. C<sub>2</sub>H<sub>6</sub>O.

The density determinations gave—

$$d_{15}^{15^{\circ}} 0·8417, \quad d_{25}^{25^{\circ}} 0·8361.$$

The magnetic rotations gave—

<i>t</i> .	Sp. rotation.	Mol. rotation.
17·0°	1·0117	32·356
17·0	1·0161	32·497
18·0	1·0132	32·424
18·0	1·0118	32·376
18·0	1·0103	32·339
Average 17·6	1·0126	32·298
Less alcohol 2·780 × 8·138....		22·624
		9·674

*Triethylamine Hydrochloride.*

A nearly saturated solution of this compound was found to contain 57.26 per cent. of the pure salt. Its composition calculated from this is represented as  $\text{Et}_3\text{N}.\text{HCl} + 5.75 \text{ mol. OH}_2$ .

The density determinations gave—

$$d_{15}^{15^\circ} 1.0202, \quad d_{20}^{20^\circ} 1.0184,$$

$$d_{25}^{25^\circ} 1.0167.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
16°	1.3285	17.441
16	1.3317	17.485
16	1.3328	17.498
16	1.3351	17.528
16	1.3319	17.487
16	1.3326	17.496
16	1.3331	17.502
16	1.3318	17.473
Average 16	1.3322	17.489
		5.750
		11.739

*Tetreehylammonium Chloride.*

The solution employed was somewhat supersaturated and deposited very large transparent crystals in cold weather. Chlorine determinations showed that it contained 55.62 per cent. of the salt; it would therefore have the composition  $\text{Et}_4\text{N}.\text{Cl} + 7.333 \text{ mol. OH}_2$ .

The density determinations gave—

$$d_{8}^{8^\circ} 1.0358, \quad d_{15}^{15^\circ} 1.0323,$$

$$d_{25}^{25^\circ} 1.0285.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
15·3	1·3069	20·926
15·3	1·3084	20·951
15·2	1·3094	21·016
15·2	1·3120	21·008
18·0	1·3068	20·950
18·0	1·3·39	20·902
18·0	1·3068	20·950
18·0	1·3072	20·955
Average 16·6	1·3076	20·957
Less 7·333 mol. OH <sub>2</sub> .....		7·333
Et <sub>4</sub> ·Cl = .....		13·624

*Piperidine Hydrochloride.*

The strongest solution which could be conveniently used contained 52·7 per cent. of this hydrochloride, and had the composition C<sub>5</sub>H<sub>11</sub>N.HCl + 6·055 mol. OH<sub>2</sub>.

The density determinations gave—

$$d_{\frac{1}{4}}^{15^{\circ}} 1\cdot0716, \quad d_{15^{\circ}}^{15^{\circ}} 1\cdot0677,$$

$$d_{25^{\circ}}^{25^{\circ}} 1\cdot0647.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
12·5	1·3436	16·097
12·5	1·3430	16·090
13·0	1·3430	16·097
13·5	1·3413	16·080
14·0	1·3412	16·080
Average 13·1	1·3424	16·089
Less OH <sub>2</sub> .....		6·055
C <sub>5</sub> H <sub>11</sub> N.HCl = .....		10·034

*Ammonium Bromide.*

Two solutions containing different quantities of this salt were examined. The strength of the solutions was found by bromine determinations.

*Solution I.*—This contained 40.423 per cent. of salt; its composition was, therefore,  $\text{NH}_4\text{Br} + 8.024 \text{ mol. OH}_2$ .

The density determinations gave—

$$d_{4^{\circ}}^{4^{\circ}} 1.2867, \quad d_{15^{\circ}}^{15^{\circ}} 1.2816,$$

$$d_{25^{\circ}}^{25^{\circ}} 1.2794.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
20.0°	1.7291	18.193
20.0	1.7332	18.233
20.0	1.7258	18.156
20.0	1.7252	18.149
Average 20.0	1.7283	18.183
Less $\text{OH}_2$ .....		8.024
$\text{NH}_4\text{Br} =$ .....		10.159

*Solution II.*—This contained 25 per cent. of salt; its composition was, therefore,  $\text{NH}_4\text{Br} + 16.339 \text{ mol. OH}_2$ .

The density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} 1.1586, \quad d_{25^{\circ}}^{25^{\circ}} 1.1574.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
22.0°	1.4135	26.594
22.0	1.4162	26.657
22.0	1.4147	26.629
16.5	1.4015	26.406
16.5	1.4075	26.462
16.5	1.4071	26.454
Average 19.2	1.4106	26.535
Less $\text{OH}_2$ .....		16.339
		10.196

*Ammonium Iodide.*

This salt was purified by recrystallisation from alcohol, and in this way was obtained quite white. It was dried in a vacuum. The strength of the solution used was found from iodine determinations, made by precipitation with silver nitrate. In the first preparation, the solution was filtered through paper, but it was found that this caused it to turn brown very rapidly, and made the readings of the magnetic rotations very difficult. It is much better, therefore, not to filter the solution, but to decant it if necessary.

*Solution I.*—This contained 60.44 per cent. salt =  $\text{NH}_4\text{I}$  + 5.273 mol.  $\text{OH}_2$ .

The density determinations gave—

$$d_{4^{\circ}}^{4^{\circ}} 1.6021, \quad d_{15^{\circ}}^{15^{\circ}} 1.5961,$$

$$d_{25^{\circ}}^{25^{\circ}} 1.9525.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
20.5°	3.0124	25.193
21.5	3.0115	25.191
21.5	3.0145	25.217
21.5	3.0175	25.235
Average 21.2	3.0140	25.209
Less $\text{OH}_2$ .....		5.273
$\text{NH}_4\text{I}$ = .....		19.936

*Solution II.*—This contained 58.46 per cent. of ammonium iodide; its composition was, therefore,  $\text{NH}_4\text{I}$  + 5.722 mol.  $\text{OH}_2$ .

The density determinations gave—

$$d_{10^{\circ}}^{10^{\circ}} 1.5727, \quad d_{15^{\circ}}^{15^{\circ}} 1.5701,$$

$$d_{25^{\circ}}^{25^{\circ}} 1.5665.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
14.5°	2.9277	25.688
14.5	2.9340	25.713
15.0	2.9415	25.812
15.0	2.9475	25.804
20.0	2.9331	25.747
18.0	2.9301	25.733
Average 16.1	2.9356	25.754
Less OH <sub>2</sub> .....		5.722
NH <sub>4</sub> I = .....		20.032

*Solution III.*—This contained 5.464 of salt; its composition was, therefore, NH<sub>4</sub>I + 6.685 mol. OH<sub>2</sub>.

The density determinations gave—

$$d_{15}^{15^{\circ}} 1.5122, \quad d_{25}^{25^{\circ}} 1.5090.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
20.0°	2.7332	26.672
20.0	2.7317	26.657
20.0	2.7332	26.671
20.0	2.7333	26.686
20.0	2.7264	26.621
20.0	2.7334	26.674
20.0	2.7274	26.615
Average 20.0	2.7312	26.656
Less OH <sub>2</sub> .....		6.685
NH <sub>4</sub> I = .....		19.971

*Solution IV.*—This contained 30.5 per cent. of salt; its composition was, therefore, NH<sub>4</sub>I + 18.333 mol. OH<sub>2</sub>.

The density determinations gave—

$$d_{15}^{15^{\circ}} 1.2351, \quad d_{25}^{25^{\circ}} 1.2334.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
21·0	1·7949	38·405
21·0	1·7977	38·465
22·0	1·7896	38·323
21·5	1·7909	38·394
22·0	1·7905	38·323
Average 21·5	1·7927	38·382
Less OH <sub>2</sub> .....		18·333
		20·049

*Results of the Four Solutions.*

Solution I.	60·44 per cent.....	19·936
„ II.	55·46 „ .....	20·032
„ III.	54·64 „ .....	19·971
„ IV.	30·5 „ .....	20·049
	Average.....	19·997

*Solution of Ammonium Iodide in Absolute Alcohol.*

The iodide of ammonium was well dried at 100°, and then boiled and kept with absolute alcohol some days; this was poured off and the salt twice more boiled with fresh quantities of absolute alcohol, the third solution being kept for use. The alcohol used had a density of  $d_{15}^{15^{\circ}} 0·7947^{\circ}$ . The strength of the solution was found by iodine determinations; it contained 21·10 per cent. of salt, and had the composition NH<sub>4</sub>I + 11·782 mol. C<sub>2</sub>H<sub>5</sub>O.

The density determinations gave—

$$d_{10}^{10^{\circ}} 0·9460, \quad d_{15}^{15^{\circ}} 0·9421.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
17·0°	1·2790	51·561
16·0	1·2848	51·762
16·0	1·2834	51·702
15·0	1·2848	51·730
15·0	1·2863	51·788
Average 15·8	1·2836	51·709
Less alcohol, 2·780 × 11·782 =		32·754
		18·955



*Ammonium Nitrate.*

The aqueous solution used contained 59.7 per cent. of this salt: its composition was, therefore,  $\text{NH}_4\text{NO}_3 + 3\text{OH}_2$ .

The density determinations gave—

$$d_{16}^{6^\circ} 1.2864, \quad d_{15}^{15^\circ} 1.2814,$$

$$d_{25}^{25.5^\circ} 1.27764.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
16.0	0.9117	5.315
16.0	0.9191	5.341
16.0	0.9172	5.329
16.0	0.9176	5.332
15.0	0.9127	5.302
15.0	0.9130	5.304
Average 15.6	0.9157	5.320
Less $3\text{OH}_2$ .....		3.000
		2.320

*Acid Sulphate of Ammonium.*

The solution of this salt used was slightly supersaturated; it contained 66.67 per cent. of salt, and had the composition  $\text{NH}_4\text{HSO}_4 + 3.193 \text{ mol. OH}_2$ .

The density determinations gave—

$$d_{15}^{15^\circ} 1.4429, \quad d_{25}^{25.5^\circ} 1.4387.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
18.0	1.0000	6.617
17.0	1.0061	6.656
17.0	0.9956	6.615
15.0	1.0061	6.664
15.0	1.0000	6.658
Average 16.4	1.0016	6.648
Less $\text{OH}_2$ .....		3.193
$\text{NH}_4\text{HSO}_4 =$ .....		3.455

*Ammonium Sulphate.*

An aqueous solution containing 40·00 per cent. of this salt was used; its composition was, therefore,  $(\text{NH}_4)_2\text{SO}_4 + 11\text{OH}_2$ .

The density determinations gave—

$$d_{10}^{10^\circ} 1\cdot2308, \quad d_{15}^{15^\circ} 1\cdot2296,$$

$$d_{20}^{20^\circ} 1\cdot2285.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
16·0	1·0740	16·016
14·5	1·0721	15·984
11·5	1·0754	16·023
10·5	1·0743	16·005
23·0	1·0690	15·952
23·0	1·0690	15·952
23·0	1·0695	15·958
23·0	1·0685	15·945
18·0	1·0721	15·988
Average 18·05	1·0715	15·980
Less 11OH <sub>2</sub> .....		11·000
		4·980

*Observations on the Nitrates, Nitro-compounds, and Nitrites.*

On placing the boiling points of the nitrates, nitro-compounds, and nitrites side by side, the differences between them are seen to be very remarkable, thus the nitrates, which are the more highly oxygenated compounds, do not boil at so high a temperature as the nitro-compounds, whilst the nitrites, which are isomeric with the latter, are extremely volatile: thus—

	B. p.		B. p.
Nitro-compounds....	$\text{CH}_3\cdot\text{NO}_2\ldots 101^\circ$	$\text{C}_2\text{H}_5\cdot\text{NO}_2\ldots$	$114\cdot5^\circ$
Nitrates .....	$\text{CH}_3\cdot\text{O}\cdot\text{NO}_2\ldots 65^\circ$	$\text{C}_2\text{H}_5\cdot\text{O}\cdot\text{NO}_2\ldots$	$87\cdot5^\circ$
	Difference.....		$36^\circ$
			$27^\circ$
	B. p.		B. p.
Nitro-compounds.	$\text{C}_3\text{H}_7\cdot\text{NO}_2\ldots 131^\circ$	$(\text{CH}_3)_2\text{C}_2\text{H}_4\cdot\text{NO}_2\ldots$	$140^\circ$
Nitrates .....	$\text{C}_3\text{H}_7\cdot\text{O}\cdot\text{NO}_2\ldots 110\cdot5^\circ$	$(\text{CH}_3)_2\text{C}_2\text{H}_3\cdot\text{O}\cdot\text{NO}_2\ldots$	$124^\circ$
	Difference ...		$20\cdot5^\circ$
			$16^\circ$

	B. p.		B. p.
Nitro-compounds. . . . .	$\text{CH}_3\cdot\text{NO}_2 \dots 101^\circ$	$\text{C}_2\text{H}_5\cdot\text{NO}_2 \dots 114.5^\circ$	
Nitrites . . . . .	$\text{CH}_3\cdot\text{O}\cdot\text{NO} \dots \text{Gas}$	$\text{C}_2\text{H}_5\cdot\text{O}\cdot\text{NO} \dots 17^\circ$	
	<hr/>	<hr/>	
Difference. . . . .	more than $101^\circ$	.....	$97.5^\circ$
	<hr/>		
	B. p.		B. p.
Nitro-compounds	$\text{C}_3\text{H}_7\cdot\text{NO}_2 \dots 131^\circ$	$(\text{CH}_3)_2\text{C}_2\text{H}_3\cdot\text{NO}_2 \dots 140^\circ$	
Nitrites . . . . .	$\text{C}_3\text{H}_7\cdot\text{O}\cdot\text{NO} \dots 44^\circ$	$(\text{CH}_3)_2\text{C}_2\text{H}_3\cdot\text{O}\cdot\text{NO} \dots 67.5^\circ$	
	<hr/>	<hr/>	
Difference . . . . .	$87^\circ$	.....	$72.5^\circ$

It is also worth noticing that in the lower members of the series the difference between the boiling points is greatest; thus in the comparison of the nitrites and nitro-compounds methyl nitrite is a gas, whilst the nitro-compound boils at  $101^\circ$ ; with the ethyl-compounds the diff. is  $97.5^\circ$ , in the propyl  $82^\circ$ , and in the isobutyl  $72.5^\circ$ . The same thing is seen when comparing the nitrates and nitro-compounds.

The densities do not vary in the same order as the boiling points, those of the nitrates being the highest. The nitrites, however, are considerably lower than the nitro-compounds: thus—

Ethyl nitrate. . . . .	$d_{15^\circ}^{15^\circ}$	1.1159
Nitro-ethane . . . . .	„	1.0561
Ethyl nitrite . . . . .	$d_{0^\circ}^{0^\circ}$	0.920
Isobutyl nitrate . . . . .	$d_{4^\circ}^{4^\circ}$	1.0334
Nitro-isobutane . . . . .	$0^\circ$	1.0083
Isobutyl nitrite . . . . .	$d_{4^\circ}^{4^\circ}$	0.8878

The boiling points and densities of nitro-compounds being so very much higher than those of nitrites, made it desirable to determine the molecular weight of a nitro-compound at a lower temperature than had been previously employed; Raoult's method was therefore used. The experiment was made with glacial acetic acid, 1.250 parts of nitroethane being added to the 100 parts of acid, the result obtained for the molecular weight was 80, the theoretical number being 75, therefore, notwithstanding the above peculiarities, when in the liquid state nitroethane has the same molecular weight as that found by Victor Meyer for its vapour.

*Nitric Acid.*

The specific magnetic rotation of this substance is very low, only a little more than half that of water. The small amount of water in the specimen examined would, if anything, slightly reduce the rotation, as will be seen further on, but the maximum effect it would produce could not be more than 0.004 on the molecular rotation, it may therefore be disregarded.

*Hydrated Nitric Acid.*

The acid examined contained 56.74  $\text{H}_2\text{NO}_3$ , and had the composition  $\text{HO}\cdot\text{NO}_2 + 2.670 \text{ mol. OH}_2$ . The effect of the water is to reduce the rotation, thus—

$$\begin{array}{r}
 \text{HO}\cdot\text{NO}_2 + 2.670 \text{ OH}_2 = 3.656 \\
 \text{less } 2.670 \text{ OH}_2 = 2.670 \\
 \hline
 \text{HO}\cdot\text{NO}_2 = 0.986 \\
 \text{Pure HO}\cdot\text{NO}_2 \text{ gave } 1.180 \\
 \hline
 \text{Difference} = \text{reduction} = 0.194
 \end{array}$$

It therefore appears that combination takes place as in the case of sulphuric acid (*Four. Chem. Soc.*, 1886, **49**, 783). This contraction, however, is not quite so large as would be expected from the union of 1 mol. of water with the acid, and it is very probable that for the existence of  $\text{H}_2\text{NO}_4$  a larger percentage of water may have to be present than in the acid examined, as in the case of sulphuric acid, which apparently requires at least 3 mols. of water to be added to  $\text{H}_2\text{SO}_4$  for the conversion of all the acid into  $(\text{HO})_3\text{SO}$ . The calculated molecular rotation for  $\text{H}_2\text{NO}_4$  would be about 1.930; the above result makes it 1.986. The existence of such a compound as  $(\text{HO})_3\text{N}\cdot\text{O}$  cannot be regarded as improbable, as we have an analogous compound in the case of orthophosphoric acid,  $(\text{HO})_3\text{P}\cdot\text{O}$ , and, moreover, there are several salts which correspond to  $(\text{HO})_3\text{N}\cdot\text{O}$ , as—

Trimercuric nitrate,  $\text{Hg}_3''\text{N}_2\text{O}_8$ ,  
 Tricupric nitrate,  $\text{Cu}_3''\text{N}_2\text{O}_8$ ,  
 Triplumbic nitrate,  $\text{Pb}_3''\text{N}_2\text{O}_8$ ,

though there are no nitrates of the alkali metals of this type corresponding to the alkaline ortho-phosphates.

*Nitric Ethers.*

When nitric acid is converted into a nitric ether the change which

takes place in the rotation is very similar to that of the acids of the fatty series and shows contraction, the increase of the rotation by the alcohol radical not being equal to that required for change of composition. The best compounds to compare nitric acid and its ethers with are perhaps formic acid and its ethers, as formic acid contains the smallest amount of carbon. By subtracting the molecular rotation of the acids from the rotation of the ether, the difference obtained for the changes of composition can easily be compared—

Nitrate of methyl . . . .	2.057	Formate of methyl . . .	2.495
Nitric acid . . . . .	1.180	Formic acid . . . . .	1.671
<hr/>		<hr/>	
Difference for $\text{CH}_2$ . . . .	0.877	Difference for $\text{CH}_2$ . . .	0.824
Ordinary value for $\text{CH}_2$	1.023	Ordinary value for $\text{CH}_2$	1.023
<hr/>		<hr/>	
Nitrate of ethyl . . . . .	3.084	Formate of ethyl . . . .	3.564
Nitric acid . . . . .	1.180	Formic acid . . . . .	1.671
<hr/>		<hr/>	
Difference for $\text{C}_2\text{H}_4$ . .	1.904	Difference for $\text{C}_2\text{H}_4$ . .	1.893
Ordinary value for $\text{C}_2\text{H}_4$	2.046	Ordinary value for $\text{C}_2\text{H}_4$	2.046
<hr/>		<hr/>	
Nitrate of propyl . . . . .	4.085	Formate of propyl . . . .	4.534
Nitric acid . . . . .	1.180	Formic acid . . . . .	1.671
<hr/>		<hr/>	
Difference for $\text{C}_3\text{H}_6$ . . .	2.905	Difference for $\text{C}_3\text{H}_6$ . .	2.863
Ordinary value for $\text{C}_3\text{H}_6$	3.069	Ordinary value for $\text{C}_3\text{H}_6$	3.069

From these comparisons we see how similar the behaviour of nitric acid is to that of formic acid. If acetic acid and its ethers had been taken for comparison, nearly the same amount of agreement would have been observed, so that nitric acid may be said to behave in a manner similar to a fatty acid in respect to its formation of ethers.

The only other oxygenated inorganic acid which has been examined is sulphuric acid, and this also behaves like the fatty acids in reference to its methyl ether—the only ether yet examined (*Jour. Chem. Soc.*, 1886, 49, 785)—thus:—

	Mol. rotation.
Sulphate of methyl . . . . .	4.013
Sulphuric acid . . . . .	2.315
	<hr/>
	2) 1.698
	<hr/>
$\text{CH}_2$ . . . . .	0.849
Ordinary value for $\text{CH}_2$ . . . . .	1.023

*Ethylene Nitrate. Nitroglycol, C<sub>2</sub>H<sub>4</sub>(O·NO<sub>2</sub>)<sub>2</sub>.*

The density of this substance is higher than that of ethyl nitrate, as might be expected; the difference at 15° is 0·3801 for  $d_{15}^{15^\circ}$ ; its specific rotation is slightly lower. The following comparison shows the variation between their molecular rotations:—

Ethylene nitrate .....	3·768
Ethyl nitrate.....	3·084
<hr/>	
Difference for displacement of H by $-O\cdot N \ll O$	0·684

*Nitroglycerin, C<sub>3</sub>H<sub>5</sub>(O·NO<sub>2</sub>)<sub>3</sub>.*

The sp. gr. differs from that of propyl nitrate at 15° by 0·5378 for  $d_{15}^{15^\circ}$ . The relationship of the molecular rotation of this compound to a mono- and di-nitrate will be best seen if the rotation of dinitro-trimethylene be calculated from that of dinitroethylene, and used with propyl nitrate for comparison—

		Diff.
Propyl nitrate.....	4·085	} 0·684
Trimethylene nitrate (calc.)	4·769	
Nitroglycerin .....	5·407	} 0·638

From this we see that the introduction of the second NO<sub>2</sub> has not produced quite such a large increase in the rotation as the first. This is strictly in accordance with displacements by hydroxyl (*Jour. Chem. Soc.*, 1884, **45**, 559), where the influence on the rotation gradually diminishes with the introduction of successive groups, so that the behaviour of these compounds is normal, and the results agree with the constitution usually assigned to them. Had nitroglycerin contained its nitrogen in any other combination of oxygen than as  $-O\cdot N \ll O$ , as it might if its constitution were represented as C<sub>3</sub>H<sub>2</sub>(NO<sub>2</sub>)<sub>3</sub>(OH)<sub>3</sub>, the rotation when compared with that of propyl nitrate would be abnormal.

In the case of isobutyl nitrate, the influence of the iso-group is found to assert itself. This may be seen by comparing it with the calculated rotation of the normal nitrate:—

Butyl nitrate (iso) .....	5·180
Butyl nitrate (normal).....	5·108
<hr/>	
Difference for iso-group ..	0·072

This difference is somewhat less than that usually obtained. Thus in the case of the alcohols it is about 0.144, and for paraffins, aldehydes, and ethers about 0.112 (*Jour. Chem. Soc.*, 1884, **45**, 550—551).

#### *Nitrites.*

The only compound of this class examined is isobutyl nitrite.\* This was selected as being more stable and less volatile than the lower numbers of the series. The nitrogen of this substance being united to the hydrocarbon radical by oxygen as in a nitrate, it may be considered in relation to isobutyl nitrate, thus—

	Mol. rotation.
Isobutyl nitrite .....	5.510
Isobutyl nitrate.....	5.180
	<hr/>
Difference +	0.330

The fact that isobutyl nitrite, although containing less oxygen than isobutyl nitrate, and consequently of a smaller molecular weight, has a higher molecular rotation, is very interesting, as showing that nitrogen when in an unsaturated condition affects the rotation of a substance in a similar manner to unsaturated carbon, by considerably increasing it (*Jour. Chem. Soc.*, 1884, **45**, 561). This point will be referred to again further on.

One of the reasons why nitrites have a much lower boiling point than nitrates may be due to their being unsaturated compounds, because we find in many cases that these have lower boiling points than saturated compounds. For example, vinyl chloride is a gas; ethyl chloride boils at 12.5°; dichlorethylene boils at 37°; ethylene chloride at 84°, &c.

#### *Nitro-compounds.*

These have the same empirical composition as the nitrites, but their rotations are very different, thus—

Propyl nitrite (cal.) .....	4.387
Nitropropane.....	3.819
	<hr/>
Difference —	0.568

At first sight this might be thought to be simply due to the nitrogen in nitropropane being saturated and in the nitrite unsaturated, and no doubt this is the *chief* cause of the variation; but it must be borne in mind that the structures of these two compounds

\* Since writing the above some other nitrites have been examined, which give rotations confirming that of isobutyl nitrite.

differ, the nitrogen of the nitropropane being in direct union with the carbon, whilst that of the nitrite is attached to it by the intervention of oxygen, is sufficient to account for a small part of the difference between the rotations of these bodies.

The influence of the group  $-N \begin{smallmatrix} \diagup O \\ \diagdown O \end{smallmatrix}$  when displacing the hydrogen in paraffins is very small, thus—

Nitropropane .....	3·819
Propane (cal.) .....	3·590
Difference .....	0·229

With compounds of larger rotation than the above, it acts very curiously, actually reducing them, thus chloroform has a larger rotation than nitrochloroform (chloropicrin)—

Chloroform.....	5·559
Nitrochloroform .....	5·384
Difference .....	0·175

The same thing is seen to a greater extent in the aromatic series when the nitro-compound has a much lower rotation than the hydrocarbon it is made from, and in nitroparaffins it probably reduces the value of the hydrocarbon radical.

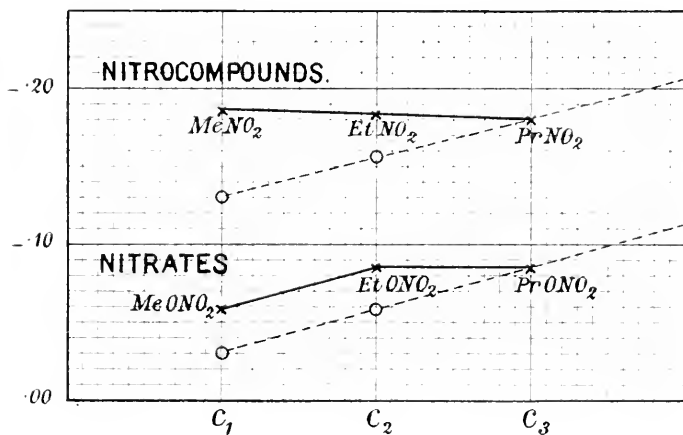
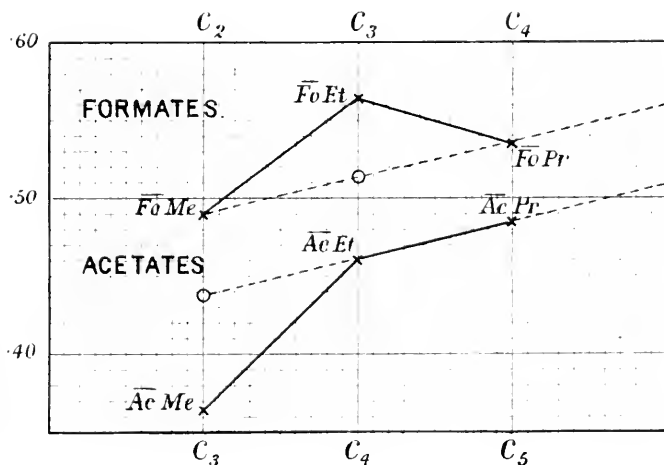
As noticed on several occasions, the magnetic rotation of the first and second members of a series of carbon compounds do not give numbers which bear the same close relationship to each other as those of the higher members, which differ regularly by 1·023. This is also seen in the case of the nitro-compounds which vary by only 0·98, and in the nitrates, which vary first by 1·025 and then by 1·00, as the following diagram will show (Fig. 1), where they are compared with the formates and acetates. The circles on the dotted lines show the positions they would occupy if they had the ordinary relationships. The ordinates in this diagram are the decimal numbers only of the molecular rotations.

*Observations on the Rotation of the Bases.*

As the values for the rotation of ammonia were obtained from its solutions in water and in alcohol, it might be objected that they are not trustworthy, as probably combination of the ammonia and the solvent might take place. It was for this reason that two different solvents were employed; alcohol being taken as one, the probability of the combination of ammonia with this liquid being less than with water. The quantities of the solutions prepared were considerable, so that on taking out samples for examination no appreciable change



FIG. 1.





of composition would take place in the bulk from loss of ammonia. It will be observed that both solutions gave practically the same rotations for ammonia, viz., 1·818 and 1·826.

It would appear, therefore, that when ammonia is absorbed either by water or by alcohol, the product simply consists of the solvent and ammonia. This is confirmed by the rotations of its nitrate and acid sulphate. I hope, however, to examine ammonia liquefied by pressure at some future time, and also other easily liquefiable gases.

The displacement of an atom of hydrogen in ammonia by an alcohol radical increases its rotation, as would be expected, but not to the full extent usual for a change of composition, which is 1·023 for every  $\text{CH}_2$  in the homologous series. This, however, is not a case quite comparable with the homologous series.

In the displacement of a second atom of hydrogen in ammonia, the rotation is increased proportionally more than by the first, and in diethylamine it is about the usual amount for the homologous series. In dipropylamine it is only a little less.

When, however, we come to the displacement of the third hydrogen, a very remarkable increase of the rotation takes place, marking out a clear distinction between diamines and triamines.

The effect of displacing a fourth atom of hydrogen by an alcohol radical in ammonium chloride is still greater than for the displacement of the third in ammonia, or, what is the same thing, in ammonium chloride; this will be seen by the following comparison:—

Tetraphylammonium chloride .....	13·624
Triethylamine hydrochloride (cal.) .....	10·005
<hr/>	
Difference for $\text{C}_2\text{H}_4$ .....	3·619

The following are the results obtained with the ethylamines and propylamines, showing the differences resulting from the displacements and between the variations of rotation. The displacement of hydrogen by  $\text{C}_2\text{H}_5$ ,  $\text{C}_3\text{H}_7$ , and  $\text{C}_4\text{H}_9$  is, of course, as far as composition is concerned, practically the same as the addition of  $\text{C}_2\text{H}_4$ ,  $\text{C}_3\text{H}_6$ , and  $\text{C}_4\text{H}_8$ .

			Molecular rotation.	Diff. for $\text{C}_2\text{H}_4$ .	Difference between rotations for each $\text{C}_2\text{H}_4$ .
Ammonia .....	N	$\left\{ \begin{array}{l} \text{H} \\ \text{H} \\ \text{H} \end{array} \right\}$	1·818		
Ethylamine .....	N	$\left\{ \begin{array}{l} \text{Et} \\ \text{H} \\ \text{H} \end{array} \right\}$	3·609	1·791	0·262
		$\left\{ \begin{array}{l} \text{H} \\ \text{Et} \end{array} \right\}$		2·053	
Diethylamine .....	N	$\left\{ \begin{array}{l} \text{Et} \\ \text{Et} \\ \text{H} \end{array} \right\}$	5·662		
		$\left\{ \begin{array}{l} \text{H} \\ \text{Et} \end{array} \right\}$		2·856	0·803
Triethylamine. ....	N	$\left\{ \begin{array}{l} \text{Et} \\ \text{Et} \\ \text{Et} \end{array} \right\}$	8·518		

			Molecular rotation.	Diff. for $C_3H_6$ .	Difference between rotations for each $C_3H_6$ .
Ammonia.....	N	$\begin{cases} H \\ H \\ H \end{cases}$	1·818	2·745	0·241
Propylamine.....	N	$\begin{cases} H \\ H \\ Pr \end{cases}$	4·563		
Dipropylamine .....	N	$\begin{cases} H \\ Pr \end{cases}$	7·549	2·986	1·129
		$\begin{cases} H \\ Pr \end{cases}$		4·115	
Tripropylamine .....	N	$\begin{cases} Pr \\ Pr \\ Pr \end{cases}$	11·664		

So that, whilst the variation of the rotations for  $C_2H_4$  between ethylamine and diethylamine differs by only 0·262, those between diethylamine and triethylamine differ by no less than 0·803; between propylamine and dipropylamine, the variation of the rotation for  $C_3H_6$  is only 0·241, yet between dipropylamine and tripropylamine it amounts to 1·129.

The relationships of the rotations of the ethylamines and propylamines amongst themselves and to each other will be more clearly understood by reference to Fig. 2, where they are represented graphically.

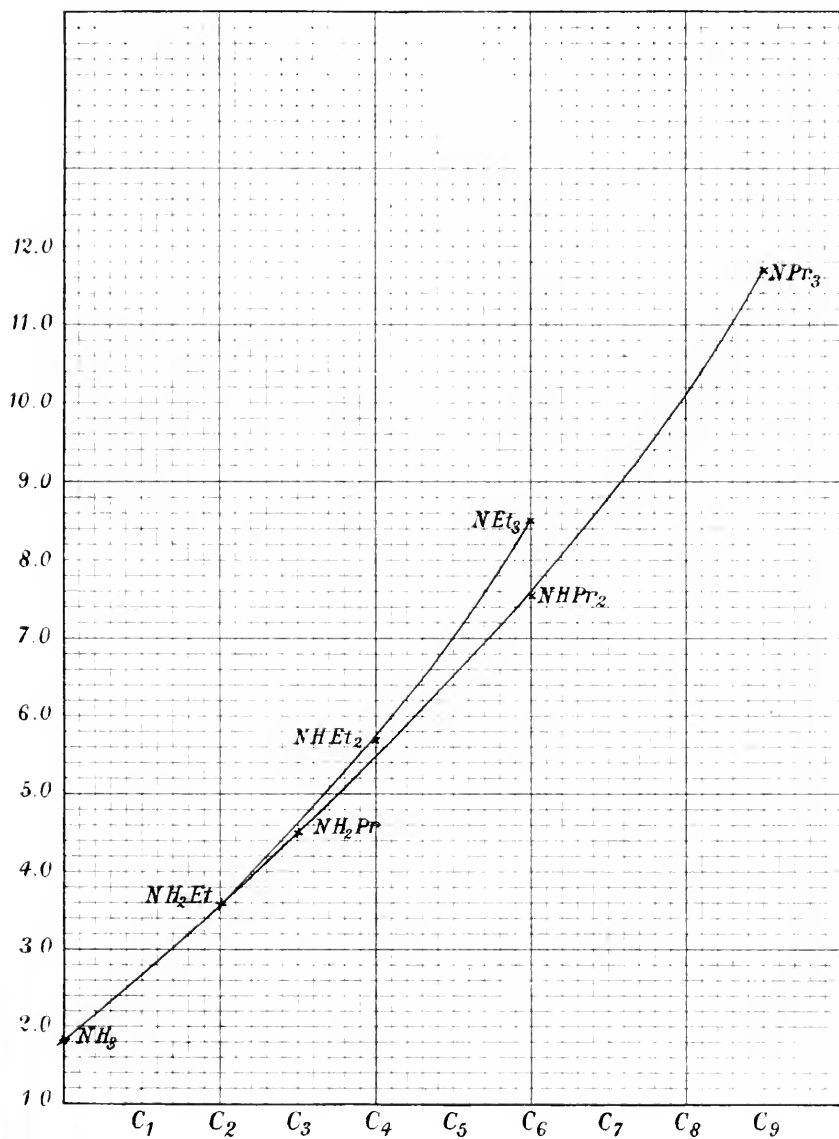
In case of the displacement with *isobutyl*, the examination of the first two only have been made, but they give results much the same as in the other cases. They are, however, interesting as showing that the iso-radicals, as compared with the normal, still exert their peculiar influence on the rotation. The following is a comparison of the results obtained with these substances:—

			Molecular rotation.	Diff. for $C_4H_8$ (Iso).	
Ammonia.....	N	$\begin{cases} H \\ H \\ H \end{cases}$	1·818	3·874	0·370
Isobutylamine.....	N	$\begin{cases} H \\ H \\ Bu \end{cases}$	5·692		
Diisobutylamine.....	N	$\begin{cases} H \\ Bu \end{cases}$	9·936	4·244	
		$\begin{cases} Bu \\ H \end{cases}$			

To get the true effect of the iso-group on the rotations of these bases, it would be necessary to compare them with the normal butylamines, but these have not been examined; it can be shown, though not very accurately, by comparing them with the propylamines, in which case the difference between them should be greater than that for the value of  $CH_2$ ; this will be found to be the case, thus—

FIG. 2.

CURVES FORMED BY THE ROTATION OF ETHYLAMINES AND  
PROPYLAMINES.





Isobutylamine .....	5.692
Propylamine .....	4.563
	<hr/>
	1.129
Difference for CH <sub>2</sub> .....	1.023
	<hr/>
Difference for iso-group. ....	0.106
Diisobutylamine .....	9.936
Dipropylamine .....	7.549
	<hr/>
	2.387
Difference for CH <sub>2</sub> × 2.....	2.046
	<hr/>
Difference for two iso-groups	0.341

These numbers are as close as could be expected by this method of comparison, and clearly show that this iso-group influences the rotations of amines in the same manner as it does other classes of compounds.

The results produced by the displacement of the hydrogen of ammonia by alcohol radicals stand alone; the only other analogous cases occur in the displacement of the hydrogens in water by ethyl, when the rotations increasingly rise with each, much as in the two first displacements in ammonia, thus—

		Molecular rotation.		Difference.
Water .....	O { $\begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix}$	1.000	} 1.780	0.217
Ethyl alcohol .....	O { $\begin{smallmatrix} \text{Et} \\ \text{H} \end{smallmatrix}$	2.780		
Ethyl oxide.....	O { $\begin{smallmatrix} \text{Et} \\ \text{Et} \end{smallmatrix}$	4.777		

And when the hydrogen in the methyl of methyl alcohol is displaced by methyl, but although we at first get an increase in the rotation of this group for the first and second displacements, the analogy with ammonia then fails, as the introduction of a third atom of methyl does not increase the rotation to the same extent as the others do.

		Molecular rotation.		Difference.
Methyl alcohol.....	HOC { $\begin{smallmatrix} \text{H} \\ \text{H} \\ \text{H} \end{smallmatrix}$	1.640	} 1.140	0.099
Ethyl alcohol .....	HOC { $\begin{smallmatrix} \text{Me} \\ \text{H} \\ \text{H} \end{smallmatrix}$	2.780		
Isopropyl alcohol.....	HOC { $\begin{smallmatrix} \text{Me} \\ \text{Me} \\ \text{H} \end{smallmatrix}$	4.019	} 1.239	-0.136
Tertiary butyl alcohol ....	HOC { $\begin{smallmatrix} \text{Me} \\ \text{Me} \\ \text{Me} \end{smallmatrix}$	5.122		

In *allylamine* we have an example of an unsaturated radical displacing the hydrogen of ammonia; as in the other cases, this being a first displacement, the radical does not increase the rotation to the same extent it usually does in other classes of compounds, thus—

			Increase due to $C_3H_5$ .
Ammonia.....	N	$\left\{ \begin{array}{l} H \\ H \\ H \\ Al \end{array} \right.$	$\left. \begin{array}{l} 1.818 \\ \\ \\ 5.587 \end{array} \right\}$
Allylamine .....	N	$\left\{ \begin{array}{l} H \\ H \\ H \end{array} \right.$	$\left. \begin{array}{l} \\ \\ \\ 5.587 \end{array} \right\}$
Allylacetic acid.....			6.426
Acetic acid.....			2.525
			<hr/>
		Increase due to $C_3H_5$ ..	3.901
Ethyl allylacetoacetate .....			10.382
Ethyl acetoacetate .....			6.501
			<hr/>
		Increase due to $C_3H_5$ ..	3.881
Ethyl allylmalonate .....			11.281
Ethyl malonate .....			7.410
			<hr/>
		Increase due to $C_3H_5$ ..	3.871

If compared with propylamine, the increase due to the radical being unsaturated will be seen—

Allylamine .....	5.587
Propylamine.....	4.563
	<hr/>
Difference.....	1.024

This is about the usual difference, although it is a little larger than is usually found for compounds containing allyl.

Pentamethylenediamine is a useful example of the successive displacements of hydrogen by  $NH_2$  in paraffins. This can be seen by comparing its rotation with that of amylamine and then again with pentane.

		Difference for displacement of H by $NH_2$ .
Pentane .....	5.638	} 0.971
Amylamine (calculated) .	6.609	
Pentamethylenediamine..	7.492	} 0.883

From this it is seen that the second displacement produces rather



less effect on the rotation than the first; this we find to be the case in other displacements in the paraffins, as in the hydroxyls of glycerin previously referred to, &c.

Before considering the rotations of piperidine and pyridine, it will be as well to consider those of the two nitriles, propionitrile and glutaric nitrile (cyanide of trimethylene). To compare these compounds it will be the simplest plan to add 1.023 to the rotation of propionitrile, which will give the value of butyronitrile, viz.,  $1.023 + 3.331 = 4.354$ , and both numbers will then be related to compounds of the same hydrocarbon; we then get the following comparisons:—

Propane (calculated) . . . . .	3.590	}	0.764
Butyronitrile (calculated). . . . .	4.354		
Glutryonitrile . . . . .	5.136	}	0.782
Average . . . . .			<hr/> 0.773

In this case the first and second displacements by CN give nearly the same numbers, the second being slightly the higher; this is exceptional in compounds of this class, and may possibly be due to some slight impurity in the glutryonitril: the numbers, however, cannot be far from the truth.

*Piperidine.*—The magnetic rotation of this base is very low, showing clearly that it is a saturated compound. The following is a comparison of it with amylamine, which contains two atoms more hydrogen:—

Amylamine . . . . .	6.609
Piperidine . . . . .	5.810
	<hr/> 0.799

This is a rather larger difference than is usually found between a saturated fatty compound and a saturated *ring* compound, and is more than the value of  $H_2(0.508)$  by which they differ.

A number of ring compounds discovered by my son have had their magnetic rotation determined, and will show this; those containing a methyl group will require to have the usual amount deducted from them, as it has been shown that this increases the rotation by about 0.111, as in iso- and secondary compounds.

Valeric acid, $C_5H_{10}O_2$ . . . . .	5.513
Tetramethylene-carboxylic acid, $C_5H_8O_2$ . . . . .	5.049
Difference . . . . .	<hr/> 0.464

Enanthylic acid, $C_7H_{14}O_2$ .....	7.552
Methylpentamethylenecarboxylic acid, $C_7H_{12}O_2$ ..	6.928
	<hr/>
Less .....	0.624
	<hr/>
Difference .....	0.111
	<hr/>
Difference .....	0.513
Caprylic acid, $C_8H_{16}O_2$ .....	8.565
Methylhexamethylenecarboxylic acid, $C_8H_{14}O_2$ ..	7.974
	<hr/>
	0.591
Less .....	0.111
	<hr/>
Difference .....	0.480
Ethyl propylmalonate, $C_6H_8O_4Et_2$ .....	10.370
Ethyl tetramethylenecarboxylate, $C_6H_6O_4Et_2$ . .	9.940
	<hr/>
Difference .....	0.430

The average of these differences is 0.471, not very far from the value of  $H_2$  by which they differ, but only a little more than half the difference found between amylamine and piperidine; in this case, however, we are dealing with a base, and it has been seen that substances of this class are somewhat exceptional in their behaviour; this, therefore, may be the cause of the variation.

*Pyridine* has also a very low rotation if considered in relation to aniline, from which it differs only by  $CH_2$ , thus—

Aniline .....	16.162
Pyridine .....	8.761
	<hr/>
Difference....	7.401

in fact, it is lower than benzene, from which it differs only by having N substituted for CH, and the value of this element as  $N'''$  is not very different from that of CH (see p. 738).

Benzene .....	11.297
Pyridine .....	8.761
	<hr/>
	2.536
Less for H ....	0.254
	<hr/>
Difference.....	2.282

This is very remarkable, especially when we find that the introduction of  $NH_2$  into benzene increases its rotation so much.

Aniline .....	16.162
Benzene .....	11.297
<hr/>	
Influence of $\text{NH}_2$	4.865

By comparing pyridine with piperidine the effect of the difference of  $\text{H}_2$ , by which they vary in composition, will be seen.

Pyridine .....	8.761
Piperidine .....	5.810
<hr/>	
	2.951

This shows how much the higher of the two the rotation of pyridine is, through being an unsaturated compound, although of less molecular weight than piperidine. This is not very far from three times the difference existing between saturated and unsaturated compounds differing from each other by  $\text{H}_2$ .

*Isobutylamine with Water and Alcohol.*—As aqueous and alcoholic ammonia appear to be simply solutions of  $\text{NH}_3$  in these solvents, it was thought that it would be well to see if a monamine acted in the same way. Solutions consisting of equal volumes of isobutylamine and water, and isobutylamine and alcohol, at  $15^\circ$ , were therefore made; in both cases heat was evolved and contraction took place; the latter will be seen by a comparison of the found and calculated densities of these mixtures.

*Water and Isobutylamine.*

Density found .....	0.9002
Average density .....	0.8681
<hr/>	
Difference due to contraction ...	0.0321

*Alcohol (absolute) and Isobutylamine (the mean of two preparations).*

Density found .....	0.7791
Average density .....	0.7656
<hr/>	
Difference due to contraction....	0.0135

On comparing the magnetic rotations of these mixtures, it will be found that a small amount of combination is indicated.

*Equal Volumes of Water and Isobutylamine.*

Molecular rotation of mixture calculated	
from constituents .....	11.200
Molecular rotation of mixture found .....	11.099
<hr/>	
Difference .....	0.101

*Equal Volumes of Alcohol and Isobutylamine.*

Molecular rotation of mixture calculated	
from constituents.....	10·459
Molecular rotation of mixture found.....	10·361
	<hr/>
Difference.....	0·098

*Piperidine and Water.*—This base has a great attraction for water, and considerable heat is evolved on mixing these two substances.

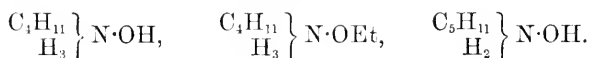
The mixture examined had the composition  $C_5H_{11}N + OH_2$ . The following is a comparison of the average and found densities of the mixture:—

Density found .....	0·9133
Average density .....	0·8897
	<hr/>
Difference due to contraction...	0·0236

This is a considerable contraction for the small quantity of water used, viz., 17·07 per cent. The magnetic rotation of this also shows a small amount of combination.

Molecular rotation of mixture calculated	
from constituents.....	6·810
Molecular rotation found .....	6·724
	<hr/>
Difference .....	0·086

The rotation of isobutylamine with water and alcohol, and of piperidine with water, therefore indicates that these mixtures contain a small quantity of unstable compounds, of the composition—



the amount most probably varying with the temperature, as was found in the examination of mixtures of aldehyde with water and alcohol (*Jour. Chem. Soc.*, 1887, **51**, 815—819), and of course may be the case with solutions of ammonia, but, if so, the amount entering into combination at the temperatures at which the rotations were observed was too small to appreciably affect them.

*Value of Nitrogen.*

From the foregoing results it is possible to get an estimate of the amount of influence nitrogen has on the magnetic rotation of bodies. In the first place, it will be as well to consider it as it exists in

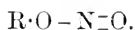
*nitrates*, where it is in a pentavalent condition. If these bodies have the composition  $\text{RO} - \text{N} \ll \text{O}$ , it will be necessary to subtract from a nitrate, the value of the radical, also that of one oxygen as found in the hydroxyl of acids, namely, 0.137, and for the two oxygens which are fully saturated with nitrogen, that is the values which this element has when fully saturated with carbon, viz., 0.261, which is probably the same as if saturated with nitrogen. We then get from ethyl and propyl nitrates the following results:—

Ethyl nitrate .....	3.084	
Ethyl .....	2.300	} 2.959
O <sub>2</sub> saturated by N.....	0.522	
O in hydroxyl of acids..	0.137	
		-----
N <sup>v</sup> .....	0.125	
Propyl nitrate .....	4.085	
Propyl .....	3.323	} 3.982
O <sub>2</sub> .....	0.522	
O .....	0.137	
		-----
N <sup>v</sup> .....	0.103	

These numbers are not far apart, and show that the value of nitrogen when saturated is very low, namely, about 0.114.

This method of calculation cannot be satisfactorily applied to nitro-compounds, because we have no very definite information as to the effect produced on the rotation when  $-\text{N} \ll \text{O}$  is in direct union with the carbon of an alcohol radical, except that it appears to reduce the value of the hydrocarbon radical to a small extent.

In the *nitrites* the nitrogen is trivalent. We can get a value for it in a similar manner to that used with nitrates, taking the constitution to be



It will be more simple, and perhaps more correct, if the rotation of propyl nitrite be used in this estimation; this is easily obtained from that of isobutyl nitrite, by adding to the rotation of propyl nitrate the difference found between isobutyl nitrite and nitrate; this is 0.330. Propyl nitrite will therefore be 4.085 (propyl nitrate) + 0.330 = 4.415.

Propyl nitrite .....	4.415	
Propyl .....	3.323	} 3.721
O saturated with N.....	0.261	
O as in hydroxyl of acids.....	0.137	
		<hr/>
N''' .....	0.694	

The rotation of nitrogen in bases can be found approximately by subtracting the rotation of a paraffin from a base and then the value of H from the remainder.

Amylamine (calculated) .....	6.609	
Pentane .....	5.638	
		<hr/>
NH.....	0.971	
Less H .....	0.254	
		<hr/>
N''' .....	0.717	

The cyanides also can be used to give a value, thus—

Ethyl cyanide .....	} 3.331	
Isopronitryl .....		
Less ethyl .....	2.300	
		<hr/>
CN .....	1.031	
Less C .....	0.515	
		<hr/>
N''' .....	0.516	

Taking trimethylene cyanide we get—

Trimethylene cyanide .....	5.136	
Trimethylene, $\text{CH}_2 \times 3$ .....	3.069	
		<hr/>
$(\text{CN})_2$ .....	2.067	
Less $\text{C}_2$ .....	1.030	
		<hr/>
$\text{N}_2$ '''.....	1.037	
N''' .....	0.518	

Average value of  $\text{N}''' = 0.611$ .

In the cyanides the value comes a little lower than in the other products, but it is possible that the value of carbon subtracted is not quite correct, as we do not know its true value when three-fourths saturated with nitrogen; though of course in all the values found for the elements they are only approximate and not absolute, as they are found to vary slightly in different series of compounds, and in some instances they vary considerably. These numbers, however, show the

interesting fact that unsaturated nitrogen ( $N'''$ ) has a very much greater influence on the magnetic rotation of compounds containing it than when it is saturated ( $N^V$ ); this is about 0.5, taking the average of all the values given, and practically half the amount of the difference usually found between saturated and unsaturated carbon compounds (differing by  $H_2$ ).

The clearest evidence of this is, perhaps, after all, best seen in the comparison between a nitrite and nitro-compound, where both have the same composition, the variation due to difference of constitution probably not reducing the rotation of the nitro-compounds by more than about 0.1; this would then leave 0.468 between these compounds in favour of  $N'''$  over  $N^V$ .

### *Hydrochloric, Hydrobromic, and Hydriodic Acids.*

When studying the magnetic rotations of the aqueous solutions of these acids, one striking fact is noticed, and that is the magnitude of the numbers as compared with those deduced from the rotations of the chlorides, bromides, and iodides of the alcohol radicals. The latter, however, refer to the acid in combination, and not in the free state, but the addition to them of about 0.2 will make the necessary correction for this. The numbers are as follows:—

		In combina- tion.	In free state.
Hydrochloric acid ..	Cl	$1.733 + H\ 0.254 = 1.987$	2.187
Hydrobromic     ,, ..	Br	$3.562 + H\ 0.254 = 3.816$	4.016
Hydriodic         ,, ..	I	$7.757 + H\ 0.254 = 8.011$	8.211

Concentrated aqueous solutions of these acids were first examined, and these gave molecular rotations for the pure acids nearly twice as large as the above; a more dilute solution of one of the acids was then examined, and this gave a still higher result, and it soon became evident that acids in different states of concentration gave different results; it appears necessary, therefore, to examine a graduated series of each acid, commencing with very concentrated and finishing with dilute solutions. The following are the results obtained:—

			Mol. rotation of HCl.
Hydrochloric acid ....	41.70 per cent.	HCl	4.045
,,       ....	36.5	,,       ,,	4.215
,,       ....	30.86	,,       ,,	4.303
,,       ....	25.60	,,       ,,	4.405
,,       ....	15.63	,,       ,,	4.419

				Mol. rotation of HBr.
Hydrobromic acid	....	65.59	per cent. HBr	7.669
"	....	56.00	" "	8.061
"	....	39.71	" "	8.415
"	....	24.60	" "	8.547
"	....	15.47	" "	8.519

				Mol. rotation of HI.
Hydriodic acid	.....	67.02	per cent. HI	17.769
"	.....	65.10	" "	17.868
"	.....	61.97	" "	18.117
"	.....	56.78	" "	18.308
"	.....	42.70	" "	18.403
"	.....	31.77	" "	18.451
"	.....	20.77	" "	18.428

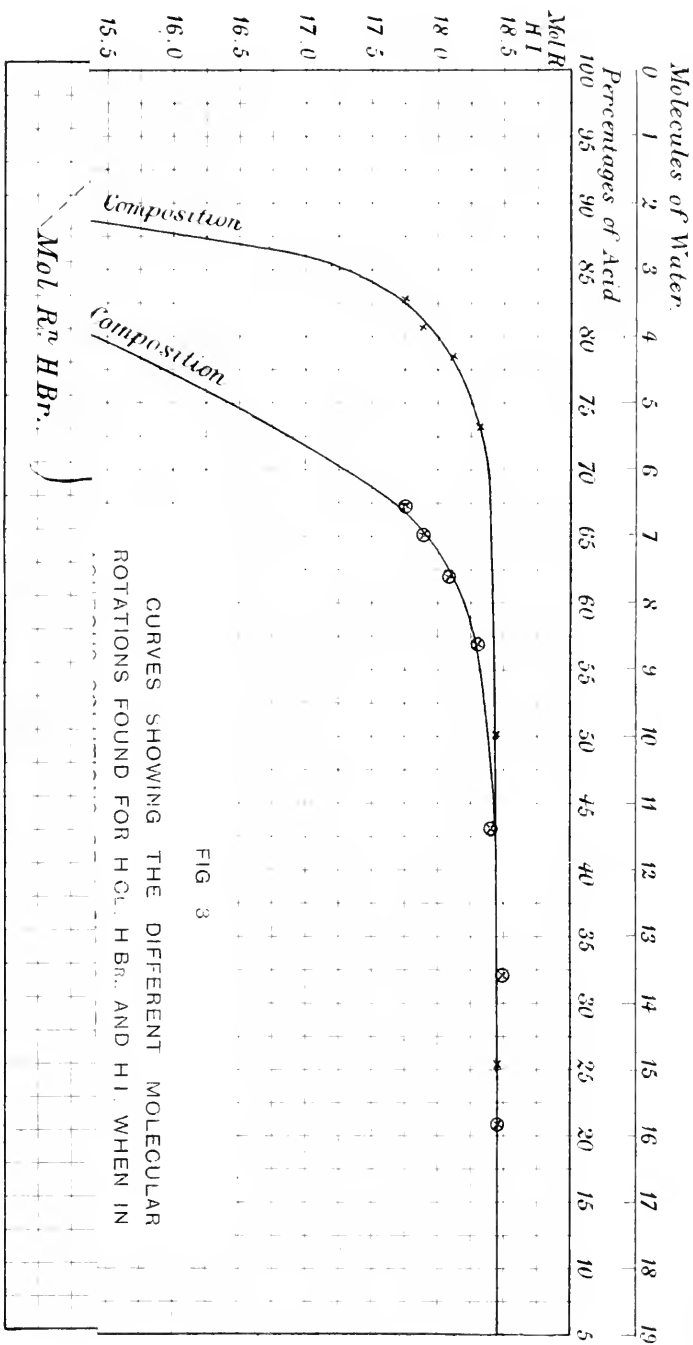
In all these series it is seen that the molecular rotations found for the pure acids first rise as the solution is diluted, and then become practically stationary, the variations of the last two numbers in each series not being more than might be expected from experimental errors.

These results have been graphically represented on Fig. 3; in this, two curves start from the calculated values of each acid, one representing the rotations in reference to the percentage of the acids, the other in reference to the molecular composition of the solution. The registers for these are both given on the top of the diagram, whilst those for the rotations are given in three columns, one on the left side and two on the right side, each headed with the formula of the acid it refers to. This arrangement was adopted to get the three sets of curves as nearly as possible in juxtaposition. It will be noticed how great a similarity there is in the character of these curves, especially those corresponding to the molecular proportions; each rising rapidly from the calculated rotations of the acids and then gradually turning off to a horizontal line. The difference of the highest rotation, represented by the horizontal lines, from the calculated is in all cases more than twice as large as the latter, thus—

	HCl.	HBr.	HI.
Highest number	4.412	8.533	18.435
Calculated number	2.187	4.016	8.211
Difference	2.225	4.517	10.224

All the rotations of these acids closely approach the horizontal line,







and therefore their highest rotations, when they contain from 6 to 7 mols. of water.

It is very difficult to form a conception of the meaning of these results, so far as experiments have gone. Acids when diluted with water either combine with it, and thus cause a reduction in the rotation, as sulphuric (*J. Chem. Soc.*, 1886, **49**, 782—784) and nitric acids, or are not influenced by it, as in the case of formic, acetic, propionic (*J. Chem. Soc.*, 1886, **49**, 778—781), glutaric acids, &c., but in no case does an increase take place; such a result would indicate dissociation. It was thought that something of this kind might take place, the very concentrated acids possibly containing complex molecules built up of several molecules of the acids, and breaking down on dilution; thus the highest rotations would be the correct ones for the simple acids, but the difficulty in the way of this is that in compounds in which the halogens must exist in single atoms the rotations of the acids deduced from them are only half those found in the examination of the dilute solutions. On account of the difficulty of finding an explanation, experiments were made to see if the solvent played any part in this matter; it was, however, found very difficult to get a liquid which would dissolve these acids in sufficient quantity, and at the same time not to be affected by them. Acetic anhydride, for example, was found to change rapidly into acetic acid and acetyl chloride, or bromide, according as it was saturated with hydrochloric or hydrobromic acids. Heptane was found to be only capable of dissolving about 1 per cent. of hydrochloric acid. At last isoamyl oxide was tried, and this dissolved about 18 per cent. of hydrobromic acid and 13 per cent. of hydrochloric acid. Unfortunately hydrobromic acid was found to gradually act upon it, so that it could not be examined in this solvent. Hydrochloric acid, however, has no influence upon it. Its solution in this substance was therefore examined. Two preparations were made, and these gave the following results:—

	Mol. rotation. HCl.
I. Containing 10·68 per cent. HCl gave .....	2·211
II.     "      12·82     "      "      .....	2·265
Average.....	2·238
Calculated rotation .....	2·187
Difference .....	0·051

These two results are very interesting, as they are quite different from those obtained on the examination of aqueous solutions, and are

as close to the calculated as could be expected, considering the small percentage of acid contained in the specimens measured. No doubt if hydrobromic and hydriodic acids could have been examined in the same way analogous results would have been obtained. It appears therefore that the calculated numbers for the halogen acids are practically the correct ones, and that the high results obtained from the aqueous acids are *abnormal*, and in some unaccountable way caused by the presence of water, though, as already mentioned, chemical union with water would not increase, but reduce the rotations of the acid, according to all previous experiments.

G. Lemoine (*Ann. Chem. Phys.* [5], **12**, 239), as well as Bertholet, have noticed the peculiar fact that, whilst gaseous hydriodic acid is decomposed by light the aqueous solutions are not, this seems to indicate that water has some peculiar influence upon this acid.

*Salts of Ammonia and Compound Ammonias.*

The results of the examination of the solutions of the salts of ammonia and the compound ammonias containing hydrochloric, hydrobromic, and hydriodic acids are not less remarkable than those of the acids themselves, except that the effect of various degrees of dilution does not influence the molecular rotation of the salts; this will be seen from the results of the examination of the four aqueous solutions of ammonium iodide and the two of ammonium bromide, as given in the following tables:—

			Mol. rotation. NH <sub>4</sub> I.
I.	NH <sub>4</sub> I,	60.44 per cent.....	19.936
II.	„	58.46 „ .....	20.032
III.	„	54.64 „ .....	19.971
IV.	„	30.50 „ .....	20.049

Average .....	19.996
---------------	--------

			Mol. rotation. NH <sub>4</sub> Br.
I.	NH <sub>4</sub> Br,	40.42 per cent.....	10.159
II.	„	25.00 „ .....	10.196
Average .....			10.177

From these it will be seen that although the solutions vary very considerably in strength, yet they give numbers which are practically the same in both instances. This fact should be borne in mind when

considering the results of the examination of the aqueous solutions of other salts referred to in this paper.

On considering the rotations obtained with solutions of the different salts formed by ammonia and the compound ammonias with the halogen acids, it will be useful to find what their calculated rotations are, so as to compare them.

The rotation of the acids taken in this place will have to be those found for them in combination, already given on page 739, then, as ammonia and the compound ammonias contain unsaturated nitrogen which will become saturated on their union with the above acids, this, as shown elsewhere, will reduce the rotation by about 0.5. The rotations of these salts may then be calculated thus :—

			Calculated.	Found.
$\text{N}_4\text{HCl}$	$= \text{HCl } 1.987 + \text{NH}_3$	$1.818 - 0.5 \dots\dots$	4.305	6.096
$\text{NH}_2\text{EtHCl}$	$= \text{HCl } 1.987 + \text{NH}_2\text{Et}$	$3.609 - 0.5 \dots\dots$	6.096	7.997
$\text{NHEt}_2\text{HCl}$	$= \text{HCl } 1.987 + \text{NHEt}_2$	$5.662 - 0.5 \dots\dots$	8.149	9.893
$\text{NEt}_3\text{HCl}$	$= \text{HCl } 1.987 + \text{NEt}_3$	$8.518 - 0.5 \dots\dots$	11.005	11.739
$\text{C}_5\text{H}_{11}\text{NHCl}$	$= \text{HCl } 1.987 + \text{C}_5\text{H}_{11}\text{N}$	$5.810 - 0.5 \dots\dots$	8.297	10.034
$\text{NH}_4\text{Br}$	$= \text{HBr } 3.816 + \text{NH}_3$	$1.818 - 0.5 \dots\dots$	6.134	10.177
$\text{NH}_4\text{I}$	$= \text{HI } 8.011 + \text{NH}_3$	$1.818 - 0.5 \dots\dots$	10.329	19.996

From the above it will be seen that the experimental results are greatly in excess of the calculated, and on examining them they are found to be nearly equal to those which would result from simply adding together the rotations of the bases, and the highest or *abnormal* rotations of the acids, no allowance being made for combination or saturation of nitrogen :—

	Abnormal rotation.		Calculated.	Found.
$\text{NH}_4\text{Cl}$	$= \text{HCl } 4.412 + \text{NH}_3$	$1.818 \dots\dots\dots$	6.230	6.096
$\text{NH}_2\text{EtHCl}$	$= \text{HCl } 4.412 + \text{NH}_2\text{Et}$	$3.609 \dots\dots\dots$	8.021	7.997
$\text{NHEt}_2\text{HCl}$	$= \text{HCl } 4.412 + \text{NHEt}_2$	$5.662 \dots\dots\dots$	10.074	9.896
$\text{NEt}_3\text{HCl}$	$= \text{HCl } 4.412 + \text{NEt}_3$	$8.518 \dots\dots\dots$	12.930	11.739
$\text{C}_5\text{H}_{11}\text{NHCl}$	$= \text{HCl } 4.412 + \text{C}_5\text{H}_{11}\text{N}$	$5.810 \dots\dots\dots$	10.222	10.034
$\text{NH}_4\text{Br}$	$= \text{HBr } 8.533 + \text{NH}_3$	$1.818 \dots\dots\dots$	10.351	10.177
$\text{NH}_4\text{I}$	$= \text{HI } 18.436 + \text{NH}_3$	$1.818 \dots\dots\dots$	20.233	19.996

It is thus seen how little the numbers obtained in this manner vary from those found, except in the case of triethylamine hydrochloride, which will be referred to further on. The hydrochloride of piperidine, which is analogous to a diamine, behaves in the same way as salts of that class. The only explanation I can find for these remarkable results is, that these salts when in solution are almost

entirely dissociated into their acids and bases, the acids, owing to the presence of water, acquiring the high or abnormal values; the slight difference between the calculated and experimental numbers being due to the presence of a very small quantity of undissociated salt. In the case of triethylamine, the amount of dissociation is evidently considerably less than in the other salts, the third molecule of ethyl it contains adding to its stability. This is only what might be expected, as the addition of a fourth molecule yields the remarkably stable chloride of tetrethylammonium. This has also been examined, and probably does not dissociate when in solution, or only to a small extent. The rotations obtained from the chloride of tetrethylammonium and the hydrochlorides of ethylamine and ammonia have been plotted out side by side with the calculated numbers in Fig. 4. From this it will be seen that the calculated numbers form a curved line (similar to the ethylamines, Fig. 2, facing p. 739), but straightens a little between triethylamine hydrochloride and triethylammonium chloride, whilst the experimental form a straight line; the latter, owing to the dissociation of the salts, is considerably far apart from the curved line in the lower portion of the figure, but both meet at the top, at a point representing tetrethylammonium chloride. It will also be seen that the distance between the curved and straight lines is less at the points representing triethylamine hydrochloride than at those representing the other hydrochlorides, thus showing a smaller amount of dissociation.

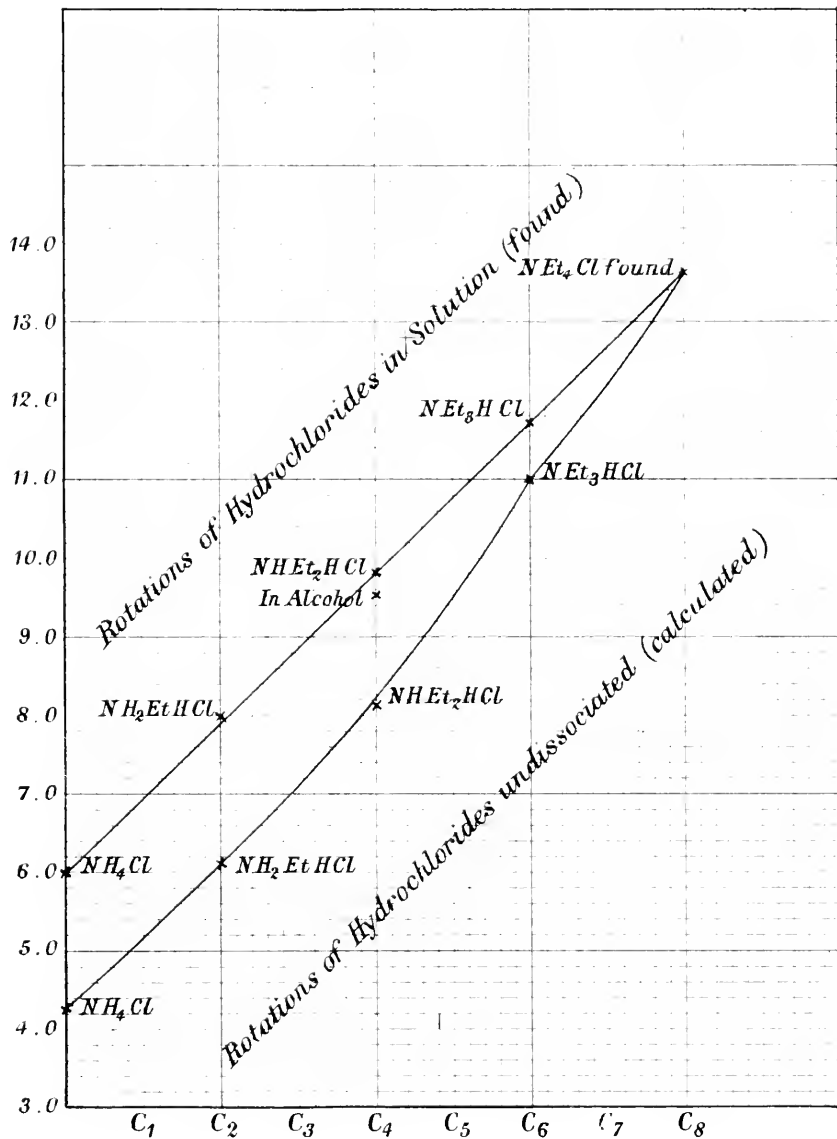
From the different results obtained from solutions of hydrochloric acid in two kinds of solvents, it appeared desirable to examine some of these salts in solvents other than water. Solutions of diethylamine hydrochloride, and ammonium iodide in absolute alcohol were therefore employed, as no other suitable solvent could be found, but from the rotations obtained dissociation evidently takes place, though not to quite so large an extent as when water is used, as the following numbers show:—

	Mol. rotation. Alcoholic solution.	Mol. rotation. Aqueous solution.	Calculated.
Diethylamine hydrochloride . . .	9.674	9.896	7.149
Ammonium iodide . . . . .	18.955	20.032	10.409

All these results made it important to study the behaviour of some other salts of ammonium when in solution, and for this purpose aqueous solutions of the nitrate, acid sulphate, and neutral sulphate of ammonium were employed. Nitrate of ammonium is not supposed to dissociate to any appreciable extent, nor is it likely that the acid sulphate would; the neutral sulphate, however, is known to do so to

FIG. 4.

CURVES SHOWING ROTATIONS INDICATING DISSOCIATION  
OF HYDROCHLORIDES WHEN IN SOLUTION.







some extent, as it gives off some of its ammonia when its solution is boiled.

The calculated rotations for these salts compared with the experimental rotation are as follows:—

*Nitrate of Ammonium.*

HNO <sub>3</sub> .....	1.180
NH <sub>3</sub> .....	1.818
<hr/>	
Less 0.2 reduction due to combination and	} 2.998
0.5 for the nitrogen being saturated =	
0.7 .....	
	<hr/>
	2.298
Found .....	2.320
	<hr/>
Difference .....	0.032

*Acid Sulphate of Ammonium.*

H <sub>2</sub> SO <sub>4</sub> .....	2.315
NH <sub>3</sub> .....	1.818
<hr/>	
	4.133
Less 0.7 as above .....	0.700
	<hr/>
	3.433
Found .....	3.455
	<hr/>
Difference .....	0.022

*Neutral Sulphate of Ammonium.*

H <sub>2</sub> SO <sub>4</sub> .....	2.315
(NH <sub>3</sub> ) <sub>2</sub> .....	3.636
<hr/>	
	5.951
Less 0.7 as above × 2 .....	1.400
	<hr/>
	4.551
Found .....	4.980
	<hr/>
Difference .....	0.431

From this it is seen that the nitrate and acid sulphate of ammonium give results very nearly identical with those calculated. This is valuable in two ways—first, inasmuch as it shows the method of calculating the rotation of these salts to be trustworthy; and, secondly,

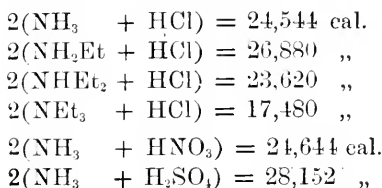
that the very high numbers obtained by the halogen acids and their salts with ammonia and compound ammonias are abnormal.

The rotation of the neutral sulphate of ammonium is rather higher than the calculated, probably the latter is a little low, as the introduction of a second ammonia would most likely be attended with a slightly smaller amount of change than that represented by 0.7; it would not, however, nearly account for all the difference found, which is no doubt due to a certain amount of dissociation of the salt.

It is very probable that the determination of the magnetic rotations of salts in solution may be of value in distinguishing between those salts that do and those that do not dissociate in the presence of water, as well as to give an idea of the extent of dissociation.

With regard to the foregoing results, it was thought that the numbers obtained for the heat of neutralisation of the salts under consideration might in some way correspond with those of the magnetic rotations; they do not appear, however, to bear in the least upon this subject, chloride of ammonium, and the hydrochlorides of the ethylamines giving numbers close to those obtained for the nitrate and sulphate of ammonium. Triethylamine hydrochloride is also a further exception, as it gives a very low number for its heat of neutralisation; this is quite contrary to the results of the magnetic rotation, which show that this salt exists in a less dissociated condition when in solution than the other hydrochlorides, and therefore would be expected to give higher numbers.

The following table gives the numbers obtained for the heat of neutralisation of most of the salts examined:—



The principal results of this research may be briefly summed up as follows:—

Nitric acid when diluted with water combines with it, forming an acid,  $\left. \begin{matrix} \text{HO} \\ \text{HO} \end{matrix} \right\} \text{N:O}$ , corresponding to orthophosphoric acid,  $\left. \begin{matrix} \text{HO} \\ \text{HO} \\ \text{HO} \end{matrix} \right\} \text{P:O}$ .

Nitric acid forms ethers in an analogous way to sulphuric and the fatty acids, that is, with condensation.

Unsaturated nitrogen,  $\text{N}'''$ , acts in a manner analogous to unsaturated carbon, the rotations of compounds in which it exists being considerably higher than those containing the saturated element.

The low rotations of nitro-compounds as compared with those of the nitrites is chiefly due to the former containing saturated and the latter unsaturated nitrogen.

That aqueous and alcoholic ammonia, at the ordinary temperature, appear to consist of solutions of  $\text{NH}_3$  only; but in the case of aqueous and alcoholic solutions of isobutylamine and aqueous solutions of piperidine a small amount of combination takes place with these solvents at ordinary temperatures.

That in the displacement of the hydrogen in ammonia by alcohol radicals the rotation is not increased by the usual amount due to the change of composition for the first, but it increases for the second, and becomes very large for the third displacement, and in the displacement of the fourth hydrogen in ammonium salts it is still larger. The introduction of iso-radicals increases the rotation more than the normal ones to quite the usual extent.

Allylamine behaves like other unsaturated compounds, giving a considerably higher rotation than the corresponding saturated base, propylamine.

Pentamethylenediamine shows that the effect of a second displacement of hydrogen in paraffins by  $\text{NH}_2$  is to produce slightly less influence on the rotation than the first.

Piperidine has a rotation showing that it is a saturated compound; it is, however, slightly lower than that usually found for saturated ring-compounds when compared with paraffin-derivatives.

Hydrochloric acid, when examined in its solution in amyl oxide, gives a rotation practically the same as that found for its elements when in compounds, that is H in paraffins and Cl in the chlorides of the alcohol radicals, with the addition necessary to represent it in the free state, 2.238 being found and 2.187 calculated.

The solutions of hydrochloric acid in water give abnormally high rotations for this acid, increasing up to certain limits with the *dilution* of the solution, the highest rotation being more than double that of the calculated.

Aqueous solutions of hydrobromic and hydriodic acids also behave in an abnormal manner, like those of hydrochloric acid, the results being rather more strongly marked. This cannot be explained on the assumption that the acids combine with water, such a result would lower instead of increase the rotation.

The rotation of ammonium salts when in aqueous solution is not influenced by the strength of the solution.

The salts of ammonia and the compound ammonias with hydrochloric, hydrobromic, and hydriodic acids when in aqueous solutions give very high rotations, which can only be explained on the assumption that they are almost entirely in a state of dissociation. Their

acids, on account of the water present, would then possess the abnormal rotations referred to above, and this would give the solutions their high values. Alcoholic solutions of ammonium iodide and diethylamine hydrochloride behave like the aqueous, but the rotations are not quite so high, showing less dissociation.

Triethylamine hydrochloride does not dissociate nearly so much as the other hydrochlorides, and the chloride of tetrethylammonium is thought not to dissociate at all, or only very slightly, when in aqueous solution.

Aqueous solutions of the nitrate and of the acid sulphate of ammonium give normal rotations, showing no appreciable amount of dissociation. The neutral sulphate, however, gives slightly high rotations, clearly indicating that it does dissociate to a small extent when dissolved in water.

The following is a list of the substances examined, with their molecular rotations, and the numbers of the pages where they are referred to in this paper:—

Substance.	Molecular rotation.	Page.
Nitric acid .....	1·180	680, 724, 725
Orthonitric acid .....	1·930	681, 724
Methyl nitrate .....	2·057	682, 722, 725
Ethyl nitrate .....	3·084	682, 722, 725
Propyl nitrate .....	4·085	683, 722, 725
Isobutyl nitrate .....	5·180	683, 722, 726
Ethylene nitrate .....	3·768	684, 726
Nitroglycerin .....	5·405	685, 726
Isobutyl nitrite .....	5·510	686, 723, 727
Nitromethane .....	1·858	687, 722, 723
Nitroethane .....	2·837	687, 722, 723
Nitropropane .....	3·819	688, 722, 727
Chloropierin .....	5·384	689, 728
Ammonia (aqueous solution) .....	1·810	689, 728
Ammonia (alcoholic solution) .....	1·826	690, 728
Ethylamine .....	3·609	691, 728
Diethylamine .....	5·662	691, 728
Triethylamine .....	8·518	692, 728
Propylamine .....	4·563	692, 730
Dipropylamine .....	7·549	693, 730
Tripropylamine .....	11·664	694, 730
Isobutylamine .....	5·692	694, 730
Isobutylamine (aqueous solution) .....	5·567	695, 735
Isobutylamine (alcoholic solution) .....	5·593	696, 735
Diisobutylamine .....	9·936	697, 730

Substance.	Molecular rotation.	Page.
Allylamine.....	5.587	697, 732
Pentamethylenediamine.....	7.192	698, 732
Piperidine.....	5.810	699, 733
Piperidine (aqueous solution).....	5.724	700, 736
Pyridine.....	8.761	700, 734
Propionitrile.....	3.331	701, 733
Trimethylene cyanide.....	5.136	702, 733
Ammonium chloride.....	6.096	712, 743
Ethylamine hydrochloride (in aqueous solution).....	7.997	713, 743
Diethylamine " " " ".....	9.896	713, 743
Diethylamine " " (in alcoholic solution).....	9.674	714, 744
Triethylamine " " (in aqueous solution).....	11.739	715, 744
Tetraphylammonium chloride " ".....	13.624	715, 729
Piperidine hydrochloride " ".....	10.034	716, 743
Ammonium nitrate " ".....	2.320	721, 745
" acid sulphate " ".....	3.455	721, 745
" sulphate " ".....	4.980	722, 745
Sulphuric acid.....	2.315	725, 745
Ammonium bromide ( $\text{NH}_4\text{Br}$ 40.42 per cent. sol.).....	10.159	716, 742
" " ( $\text{NH}_4\text{Br}$ 25 " " ).....	10.196	717, 742
Ammonium Iodide ( $\text{NH}_4\text{I}$ = 60.44 " " ).....	19.936	718, 742
" " ( $\text{NH}_4\text{I}$ = 58.46 " " ).....	20.032	718, 742
" " ( $\text{NH}_4\text{I}$ = 54.64 " " ).....	19.971	719, 742
" " ( $\text{NH}_4\text{I}$ = 30.5 " " ).....	20.049	720, 742
Ammonium Iodide in alcohol ( $\text{NH}_4\text{I}$ = 21.10 per cent.).....	18.955	720, 744
Hydrochloric acid ( $\text{HCl}$ = 41.70 per cent. sol.).....	4.015	702, 739
" " ( $\text{HCl}$ = 36.5 " " ).....	4.215	703, 739
" " ( $\text{HCl}$ = 30.86 " " ).....	4.303	703, 739
" " ( $\text{HCl}$ = 25.6 " " ).....	4.405	704, 739
" " ( $\text{HCl}$ = 15.63 " " ).....	4.419	704, 739
Hydrochloric acid in isomyl oxide ( $\text{HCl}$ = 12.82 p. e.).....	2.265	705, 741
" " " " ( $\text{HCl}$ = 10.68 " " ).....	2.211	705, 741
Hydrobromic acid ( $\text{HBr}$ = 65.59 per cent.).....	7.669	706, 740
" " ( $\text{HBr}$ = 56.0 " " ).....	8.061	706, 740
" " ( $\text{HBr}$ = 39.71 " " ).....	8.445	707, 740
" " ( $\text{HBr}$ = 24.6 " " ).....	8.547	707, 740
" " ( $\text{HBr}$ = 15.47 " " ).....	8.519	708, 740
Hydriodic acid ( $\text{HI}$ = 67.02 per cent.).....	17.769	708, 740
" " ( $\text{HI}$ = 65.1 " " ).....	17.868	709, 740
" " ( $\text{HI}$ = 61.97 " " ).....	18.117	709, 740
" " ( $\text{HI}$ = 56.78 " " ).....	18.308	710, 740
" " ( $\text{HI}$ = 42.7 " " ).....	18.403	710, 740
" " ( $\text{HI}$ = 31.77 " " ).....	18.451	711, 740
" " ( $\text{HI}$ = 20.77 " " ).....	18.428	711, 740

LXIX.—*On the Correspondence between the Magnetic Rotation and the Refraction and Dispersion of Light by Compounds containing Nitrogen.*

By J. H. GLADSTONE, Ph.D., F.R.S., and W. H. PERKIN, Ph.D., F.R.S.

The substances containing nitrogen, the magnetic rotation of which was described in Dr. Perkin's recent paper, have been examined by Dr. Gladstone with reference to their refraction and dispersion. The following table contains the refractive indices calculated from the observations.

*Liquid Substances.*

	Temp.	Sp. gr.	$\mu_A$ .	$\mu_F$ .	$\mu_H$ .
Propylamine .....	6.5°	0.7329	1.3922	1.4022	1.4111
Dipropylamine .....	4.4	0.7530	1.4086	1.4191	1.4281
Tripropylamine .....	4.4	0.7703	1.4197	1.4306	1.4408
Isobutylamine .....	6.8	0.7437	1.3999	1.4099	1.4188
Diisobutylamine .....	7.6	0.7546	1.4109	1.4211	1.4301
Allylamine .....	5.2	0.7787	1.4234	1.4377	1.4502
Methyl-aniline .....	7.8	0.9983	1.5640	1.5966	1.6324
Dimethylaniline .....	8.2	0.9675	1.5514	1.5834	1.6198
Pentamethylenediamine .....	17.5	0.8821	1.4577	1.4699	1.4803
Piperidine .....	7.0	0.8753	1.4542	1.4661	1.4757
Pyridine .....	12.2	0.9875	1.5037	1.5254	1.5468
Propionitrile .....	20.0	0.7843	1.3636	1.3723	1.3792
Trimethylene cyanide .....	24.2	0.9858	1.4315	1.4420	1.4506
Methyl nitrate .....	19.8	1.2090	1.3703	1.3809	1.3908
Ethyl „ .....	20.4	1.1078	1.3805	1.3912	1.4005
Propyl „ .....	19.6	1.0569	1.3931	1.4036	1.4134
Isobutyl „ .....	18.8	1.0165	1.3991	1.4099	1.4193
Nitroglycol .....	18.5	1.4910	1.4417	1.4550	1.4671
Nitroglycerin .....	18.6	1.5942	1.4682	1.4818	1.4945
Nitromethane .....	17.5	1.1394	1.3782	1.3898	1.4009
Nitroethane .....	20.5	1.0489	1.3875	1.3983	1.4090
Nitropropane .....	22.7	1.0022	1.3954	1.4063	1.4164
Isobutyl nitrite .....	24.2	0.8638	1.3682	1.3784	1.3838
Chloropicrin .....	17.5	1.6623	1.4577	1.4708	1.4829

In addition to these liquids, the refraction was determined of several gaseous, liquid, or solid bodies dissolved in water, namely, ethylamine, ethylamine hydrochloride, diethylamine hydrochloride, triethylamine hydrochloride, piperidine hydrochloride, hydriodic acid, ammonium iodide, ammonium nitrate, and ammonium sulphate. In each case the solution was a very strong one, so that the probable error from necessary dilution of the substance was never great.

The following table contains the molecular magnetic rotation, molecular refraction, and the molecular dispersion of the substances in question, together with those of a few others where the three properties have not been determined from the same specimen; the latter are indicated by \*.

Substance.	Formula.	Mol. mag. rotation.	Molecular refraction.	Molecular dispersion.
*Ammonia .....	$\text{NH}_3$ .....	1.810	9.03	0.50
*Ethylamine .....	$\text{NEtH}_2$ .....	3.609	24.47	1.19
*Diethylamine .....	$\text{NEt}_2\text{H}$ .....	5.662	39.36	1.96
*Triethylamine .....	$\text{NEt}_3$ .....	8.518	54.62	2.76
Propylamine .....	$\text{NPrH}_2$ .....	4.563	31.57	1.52
Dipropylamine .....	$\text{NPr}_2\text{H}$ .....	7.549	54.80	2.62
Tripropylamine .....	$\text{NPr}_3$ .....	11.664	77.91	3.92
Isobutylamine .....	$\text{NBuH}_2$ .....	5.692	39.25	1.86
Diisobutylamine .....	$\text{NBu}_2\text{H}$ .....	9.936	70.24	3.29
*Ammonium chloride .....	$\text{NH}_3\cdot\text{HCl}$ .....	6.096	22.33	1.52
Ethylamine hydrochloride ..	$\text{NEtH}_2\cdot\text{HCl}$ .....	7.997	37.18	2.06
Diethylamine „ .....	$\text{NEt}_2\text{H}\cdot\text{HCl}$ .....	9.896	51.86	2.69
Triethylamine „ .....	$\text{NEt}_3\cdot\text{HCl}$ .....	14.724	65.78	3.26
Tetreeethylammonium chloride	$\text{NEt}_4\text{Cl}$ .....	13.626	80.70	3.78
Allylamine .....	$\text{NAlH}_2$ .....	5.587	30.99	1.96
*Aniline .....	$\text{NC}_6\text{H}_7$ .....	16.162	52.99	5.96
Methylaniline .....	$\text{NC}_6\text{H}_6\text{Me}$ .....	19.629	60.45	7.33
Dimethylaniline .....	$\text{NC}_6\text{H}_5\text{Me}_2$ .....	22.823	68.96	8.55
Pentamethylene diamine ....	$(\text{NH}_2)_2(\text{CH}_2)_5$ .....	7.492	52.93	2.61
Piperidine .....	$\text{NC}_5\text{H}_{11}$ .....	5.810	44.11	2.09
„ hydrochloride ....	$\text{NC}_5\text{H}_{11}\text{HCl}$ .....	10.034	56.57	2.96
Pyridine .....	$\text{NC}_5\text{H}_5$ .....	8.761	40.30	3.44
Propionitrile .....	$\text{NC}_3\text{H}_5$ .....	3.331	25.50	1.09
Trimethylene cyanide .....	$(\text{NC})_3(\text{CH}_2)_3$ .....	5.136	41.15	1.82
Methyl nitrate .....	$\text{MeNO}_3$ .....	2.057	23.59	1.30
Ethyl „ .....	$\text{EtNO}_3$ .....	3.084	31.26	1.64
Propyl „ .....	$\text{PrNO}_3$ .....	4.085	39.05	2.02
Isobutyl „ .....	$\text{BuNO}_3$ .....	5.180	46.72	2.36
Nitroglycol .....	$\text{C}_2\text{H}_4(\text{NO}_3)_2$ .....	3.768	45.03	2.59
Nitroglycerin .....	$\text{C}_3\text{H}_5(\text{NO}_3)_3$ .....	5.405	66.67	3.74
Nitromethane .....	$\text{MeNO}_2$ .....	1.858	20.25	1.22
Nitroethane .....	$\text{EtNO}_2$ .....	2.837	27.71	1.53
Nitropropane .....	$\text{PrNO}_2$ .....	3.819	35.11	1.87
Isobutyl nitrite .....	$\text{BuNO}_2$ .....	5.510	43.90	2.35†
Chloropierin .....	$\text{CCl}_3\text{NO}_2$ .....	5.384	45.29	2.50
Hydrochloric acid (36.5 p. c.)	$\text{HCl}$ .....	4.215	14.45	1.12
Hydroiodic acid (65.1 p. c.) ..	$\text{HI}$ .....	17.868	31.87	4.19
Hydrobromic acid (dilute) ..	$\text{HBr}$ .....	8.533	20.65	2.19
Ammonium iodide .....	$\text{NH}_4\text{I}$ .....	19.878	39.66	4.88‡
*Nitric acid .....	$\text{HNO}_3$ .....	1.180	16.50	1.13
*Sulphuric acid .....	$\text{H}_2\text{SO}_4$ .....	2.315	22.37	0.97
Ammonium nitrate .....	$\text{NH}_4\text{HNO}_3$ .....	2.316	25.23	1.88
„ sulphate .....	$(\text{NH}_4)_2\text{H}_2\text{SO}_4$ .....	4.980	39.50	1.78

† Estimated from  $\mu_F$  and  $\mu_G$ .

‡ Estimated from  $\mu_F$ .

The object of this table is to draw attention to the general correspondence that exists between these three different properties of the substances in question; a correspondence that points to some connection between the rotation of the polarised ray under magnetic influence and the retardation of the rays of light in passing through a material substance.

The three columns, though expressing different properties, are really comparable with one another, for in each case the observed value is divided by the density of the substance, and it is determined not for equal weights but for an equal number of molecules. This is shown by the formulæ employed for reducing the observations.

Molecular magnetic rotation =  $\frac{r \times Mw}{r' \times Mw' \times d}$ , where  $r$ ,  $Mw$ , and  $d$

represent respectively the observed rotation, molecular weight, and density of the substance, and  $r'$  and  $Mw'$  the corresponding values for water. Molecular refraction, generally called refraction equivalent,

=  $Mw \frac{\mu_A - 1}{d}$ , and molecular dispersion, or dispersion equivalent, =

$Mw \frac{\mu_H - \mu_A}{d}$ , where  $\mu_A$  and  $\mu_H$  are the refractive indices of the lines A

and H of the solar spectrum. It has been found that each property is determined in the first instance by the atomic composition of the substance, so that it may be laid down as a primary law that the molecular magnetic rotation, refraction, or dispersion of a compound is the sum of the molecular magnetic rotation, refraction, or dispersion of its constituents. The values which have been deduced under this primary law, mainly from the paraffin-group, are, however, subject to large modifications, dependent upon differences in the structure of the compound. Thus a change of valency is attended by a marked change of value in these optical properties, and they are apparently affected by some circumstances which are not as yet recognised in our structural formulæ.

From the primary law above given, the following values have been deduced by Perkin law for the molecular rotation of certain elements in the paraffin-group of carbon-compounds, and against them have been placed the normal values for their molecular refraction and dispersion arrived at by Landolt, Brühl, and Gladstone.



	Molecular magnetic rotation.	Molecular refraction.	Molecular dispersion.
CH <sub>2</sub> .....	1.023	7.6	0.34
C .....	0.515	5.0	0.26
H .....	0.254	1.3	0.04
O, alcoholic .....	0.194	2.8	0.10
O, aldehydic .....	0.261	3.4	0.18
Cl .....	1.733	9.9	0.50
Br .....	3.562	15.3	1.22
I .....	7.757	24.5	2.62
N, in amines. ....	0.717	5.1	0.38

A glance at this table will show that the three columns are quite independent. The relative figures for one substance do not correspond with those for another, although there is a certain analogy between them.

Directly, however, that we turn to the modifications that are introduced by changes in the mode of combination, we find that when a change occurs in the one property it is noticeable also in the other two, and these changes are in the same direction, though not to the same extent; in fact, the variations in the magnetic rotation are usually greater than those in the dispersion, and these again are much more marked than in the refraction.

This was first observed by us some years ago. It struck us as a remarkable coincidence that the separate investigations showed two different values for oxygen in alcohols and aldehydes, and that there was a very great exaltation of the values in the case of unsaturated carbon-compounds, such as those containing allyl. We observed also that the value of CH<sub>2</sub> in the first and second member of the homologous series (such as the alcohols, the fatty acids, &c.) was different from its value in the higher members of the same series, and that these differences were always in the same direction. We have since noticed also that where there was an abnormally large molecular rotation, as in methylene iodide, there is an abnormally large molecular refraction and dispersion.

Nor have we been the only observers who have been aware of some connection between the two sets of phenomena. H. Becquerel, in his "Experimental Researches on Magnetic Rotatory Polarisation," printed in the *Ann. Chem. Phys.*, of 1877, drew up a table, which showed a certain rough relationship between that property and the refractive index. But as he took no account of differences in density or molecular weight, he failed to recognise the connection between these and chemical constitution.

Kaouonnikoff (*J. Russ. Chem. Soc.*, 1888) also has pointed out some curious relations between the specific rotatory and the refractive power of those chemical substances which under ordinary circumstances exhibit circular polarisation. But this kind of rotation appears to be a totally different phenomenon from that produced by exposure in a magnetic field.

The series of compounds containing nitrogen seem to afford a remarkably good opportunity for comparisons, and the results have exceeded our expectations. We propose now to consider only the more salient points, leaving the smaller questions for future consideration.

I. *Compound Ammonias*.—At the commencement of the second table will be found two good series of compound ammonias, the one resulting from the successive substitution of ethyl for hydrogen, and the other from successive substitution of propyl. The difference for the first is  $C_2H_4$ , and for the second  $C_3H_6$ , and the value of these groups is found by subtracting the figures for ammonia from those for ethylamine, ethylamine from diethylamine, &c. In every instance there is an increase, and these are given by the following table:—

	Molecular magnetic rotation.	Molecular refraction.	Molecular dispersion.
Ethyl, 1st substitution .....	1.799	15.44	0.69
„ 2nd „ .....	2.053	14.89	0.77
„ 3rd „ .....	2.856	15.26	0.80
Normal increase for $C_2H_4$ .....	2.046	15.2	0.68
Propyl, 1st substitution .....	2.753	22.54	1.02
„ 2nd „ .....	2.986	23.23	1.10
„ 3rd „ .....	4.115	23.11	1.30
Normal increase for $C_3H_6$ .....	3.069	22.8	1.02

A noteworthy fact here is the rapid augmentation of the molecular rotation for each additional  $C_2H_4$  or  $C_3H_6$ . The same is clearly indicated also in the molecular dispersion. It is doubtful in the molecular refraction, but the irregularities of the numbers are such as may be due to experimental error.

II. *Hydrochlorides of the Compound Ammonias*.—The increase for each addition of  $C_2H_4$  in this series is as follows, starting from ammonia hydrochloride:—

	Molecular magnetic rotation.	Molecular refraction.	Molecular dispersion.
Ethyl, 1st substitution .....	1.901	14.85	0.54
„ 2nd „ .....	1.899	14.68	0.63
„ 3rd „ .....	1.828	13.92	0.57
„ 4th „ .....	1.902	14.92	0.52
Normal increase for $C_2H_4$ .....	2.046	15.2	0.68

The numbers were obtained from the examination of these salts in aqueous solution.

In this series, unlike the preceding, there is no progression in the increase, the additional amounts remaining about the same in regard to the rotation, refraction, and dispersion. There is also another point of correspondence between the three optical properties. In the case of each of them the increase never amounts to the theoretical quantity.

III. *Compound Anilines*.—The short series of methylanilines gives the following increases for each addition of  $CH_3$ , starting from aniline.

	Molecular magnetic rotation.	Molecular refraction.	Molecular dispersion.
1st substitution .....	3.467	8.36	1.37
2nd „ .....	3.194	8.51	1.22
Normal increase for $CH_2$ .....	1.023	7.6	0.34

Here the increase in the molecular rotation for each  $CH_2$  is more than three times that which is usually observed in a series belonging to the paraffin group. An equally large augmentation is manifest in the molecular dispersion, and a very visible increase occurs in the refraction. This exaltation of the dispersion equivalent of  $CH_2$  in some members of the aromatic group was observed by Gladstone and Dale as far back as 1866.

IV. *Unsaturated Carbon Compounds*.—The table includes three very different examples of unsaturated carbon compounds, allylamine, pyridine, and aniline with its substitution compounds. In each case the observed value is considerably greater than that which would be calculated from the normal values for carbon, hydrogen, and ammonia in the paraffin series.

	Molecular magnetic rotation.		Molecular refraction.		Molecular dispersion.	
	Found.	Calculated.	Found.	Calculated.	Found.	Calculated.
Allylamine.....	5·587	4·040	30·99	29·23	1·96	1·44
Pyridine.....	8·761	4·562	40·30	36·63	3·44	1·88
Aniline.....	16·162	5·585	52·09	41·23	5·96	2·22

It will be observed not only that there is a great increase in each case, but that whilst in allylamine, where there is only one pair of double-linked carbon atoms, the increase is considerable, in aniline, where there are three such pairs, the increase in rotation and dispersion is about seven times as much, and in refraction the increase is more than four times as great.

V. *Nitriles compared with Ammonias*.—It was observed many years ago that the refraction equivalent of nitrogen in nitriles and cyanides was smaller than in the nitrogen bases, and this observation was recently extended to the dispersion equivalent. The second table affords two opportunities of testing this in regard to the molecular magnetic rotation, namely, propionitril and trimethylene cyanide. By subtracting the normal values for hydrogen and carbon from the observed values for these compounds we obtain the values of nitrogen.

Nitrogen.	Molecular magnetic rotation.	Molecular refraction.	Molecular dispersion.
From amines.....	0·717	4·9	0·38
„ propionitrile.....	0·516	4·0	0·11
„ trimethylene cyanide.....	0·518	4·2	0·14

VI. *Nitric Ether Series*.—There is a good homologous series in the second table, commencing with methyl nitrate. Assuming nitric acid to be the first member of the series, we obtain the following values for each addition of  $\text{CH}_2$ .

	Molecular magnetic rotation.	Molecular refraction.	Molecular dispersion.
1st addition .....	0·877	7·1	0·17
2nd    ,,    .....	1·027	7·67	0·34
3rd    ,,    .....	1·001	7·79	0·38
4th    ,,    (Isobutyl).....	1·095	7·67	0·34
Normal increase.....	1·023	7·6	0·34

Here there are two points of correspondence to be specially noted. It is evident that neither in the magnetic rotation, refraction, nor dispersion does the first addition of  $\text{CH}_2$  produce the normal increase; but whilst this normal increase is found in each of the successive additions, they are all practically alike, and there is no continuous augmentation of the increase as in the case of the compound ammonias. An exception to this last remark is, however, the increase in molecular rotation (1·095) observable in isobutylic nitrate. This, like the isocompounds in general, is somewhat higher than the normal value, a difference not perceptible in the refraction and dispersion.

VII. *Isobutyl Nitrite and Nitrate*.—Though there are several  $\text{NO}_2$  compounds in the table, there is only one true nitrite, that of isobutyl. In his paper, Dr. Perkin has drawn especial attention to the fact, that though this substance contains an atom of oxygen less than the isobutyl nitrate, it has a greater molecular magnetic rotation. This is attributed to the fact that the nitrogen is saturated in one case and not saturated in the other. The difference between the two is shown below for each of the optical properties.

	Molecular magnetic rotation.	Molecular refraction.	Molecular dispersion.
Isobutyl nitrite .....	5·510	43·90	2·35
,,    nitrate .....	5·180	46·72	2·36
Difference for O .....	−0·330	+2·82	+0·01
Normal difference .....	+0·261	+3·4	+0·18

Whilst the addition of oxygen has caused an actual diminution in the magnetic rotation, it has given only a doubtful increase in the dispersion and an increase on the refraction considerably below the normal for aldehydic oxygen. The three results, though apparently different, are in the same direction.

The nitro-compounds themselves differ from one another to the usual extent in regard to all three optical properties.

VIII. *Acids and their Ammonium Salts*.—It was among the earliest observations on refraction equivalents that the halogen acids in solution gave abnormal figures, far higher than those deducible from the compounds of the halogens with organic radicals. The same is now shown to hold good for their molecular magnetic rotation. It is also found that these values increase with the dilution of the acid up to a certain extent; and in the following tables the higher values are used. The calculated values for the magnetic rotations are for the *free* acids (see p. 739).

	Molecular magnetic rotation.		Molecular refraction.		Molecular dispersion.	
	Found.	Calculated.	Found.	Calculated.	Found.	Calculated.
Hydrochloric acid	4·412	2·187	14·45	11·2	1·12	0·54
Hydrobromic acid	8·533	4·016	20·65	16·6	2·19	1·26
Hydriodic acid ..	18·435	8·211	31·87	25·8	4·19	2·66

Dr. Perkin has shown that these acids in combining with ammonia or piperidine retain their abnormal values, and combine with but little condensation. How far this is true for the other optical properties is shown in the following table. The calculated numbers are the values of the base and acid added together.

	Molecular magnetic rotation.		Molecular refraction.		Molecular dispersion.	
	Found.	Calculated.	Found.	Calculated.	Found.	Calculated.
NH <sub>3</sub> + HCl ....	6·096	6·230	22·33	23·48	1·52	1·62
NH <sub>3</sub> + HBr. ....	10·177	10·351	28·53	29·68	2·49	2·69
NH <sub>3</sub> + HI.....	19·996	20·253	39·66	40·90	4·88	4·69
Piperidine + HCl	10·034	10·222	56·43	58·56	2·96	3·21
Triethylamine } + HCl..... }	11·739	12·930	65·78	69·07	3·26	3·88

The correspondence is again seen in these cases, and all the three optical properties indicate that although there is but little condensation in the case of ammonia and hydrochloric, hydrobromic, or hydriodic acid, yet there is considerable condensation in the case of the triethylamine-compound with hydrochloric acid.

IX. *Hydrochloric Acid in Solution*.—Although hydrochloric acid, when dissolved in water, has a far greater effect on light than could have been expected, it has recently been found that when dissolved in isoamyl oxide it rotates the plane of polarisation to very little more than the theoretical extent. On examining the refraction and dispersion, a still closer agreement with theory became manifest.

Hydrochloric acid.	Molecular magnetic rotation.	Molecular refraction.	Molecular dispersion.
In water.....	4.412	14.45	1.12
In isoamyl oxide.....	2.238	11.36	0.51
By calculation for free acid ....	2.187	11.2	0.54

These nine cases of comparison all represent different kinds of departure from what we consider the normal values. They have shown a very marked correspondence between the three optical properties of the substances examined. They have also revealed differences in detail, and it is only fair to add that other peculiarities in the molecular magnetic rotation exist which are not represented by similar peculiarities in the refraction and dispersion. But these exceptions are of such a limited character that on a re-examination of the matter with fresh specimens, and with varied conditions, it is quite conceivable that they may disappear.

It may therefore be laid down as generally, if not always, true, that where there is a departure from the normal values in regard to one or other of these properties, it is to be found in the other two. The different properties are evidently similarly affected by change in chemical constitution. The general drift of the whole comparison appears to us to lead irresistibly to the conclusion that we have here another close relationship between electro-magnetism and the velocity of light.

#### LXX.—On Phosphoryl Trifluoride.

By T. E. THORPE, F.R.S., and F. J. HAMBLY.

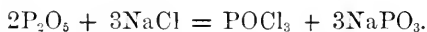
THE existence of oxyfluoride of phosphorus was first definitely established by Moissan, who obtained it by the action of the electric spark upon a mixture of phosphorus trifluoride and oxygen. On passing the induction spark into a mixture of 2 vols. of the trifluoride and 1 vol. of oxygen standing over mercury, a violent explosion occurs, and the new gas is produced. (*Compt. rend.*, **102**, 1245.)

In a paper on the Oxidation of Haloid Salts in the *Journal für praktische Chemie*, 1880, **21**, 438, Schulze has described the behaviour of various oxides upon haloid salts in absence of oxygen, and states that on heating fluorides with molybdic oxide and phosphoric oxide, oxyfluoride of molybdenum and oxyfluoride of phosphorus were obtained. No description of the properties of these compounds is given, nor do any analytical observations appear to have been made.

We find that phosphorus oxyfluoride can be easily obtained by heating an intimate mixture of cryolite and phosphorus pentoxide. The materials, in the proportion of 2 parts of the finely-powdered cryolite and 3 parts of phosphoric oxide, are placed in a brass tube and gently heated. The gas is readily disengaged, and as soon as that which is evolved is wholly absorbed by caustic soda solution, the rest may be collected at the mercurial trough. That the gas so obtained is practically pure is shown by the following numbers:—

	Observed.	Calculated.
Vapour density . . . . .	52·3	52·0
Determination of phosphorus—		
Preparation I . . . . .	30·36 p. c.	29·81
Preparation II . . . . .	30·06 „	—

This method of obtaining phosphorus oxyfluoride is analogous to that by which Kolbe and Lautemann prepared the oxychloride (*Annalen*, **113**, 240), namely, by heating phosphoric anhydride with common salt:



We had intended to have completed our study of this gas before offering any communication on the subject, but, as we are no longer in a position to work in concert, we have ventured to lay this short preliminary note before the Society. One of us, however, trusts, in a short time, to be able to present the results of a fuller investigation.

#### LXXI.—*Oxyamidosulphonates and their Conversion into Hyponitrites.*

By EDWARD DIVERS, M.D., F.R.S., and TAMEMASA HAGA, F.C.S.

IN our paper on the *Reaction between Sulphites and Nitrites of Metals other than Potassium* (TRANS., 1887, **51**, 659), we gave notice of our intention to work on the reactions with the sodium salts. This we have done, and are already in a position to materially extend and



modify our knowledge of the chemistry of the sulphazotised compounds contained in the writings of our predecessors in the investigation, Fremy (*Ann. Chim. Phys.* [3], **15**, 408), A. Claus and Koch, (*Annalen*, **152**, 336; **158**, 52 and 194), Berglund (*Bull. Soc. Chim.*, **25**, 455; *Ber.*, **9**, 252 and 1896), and Raschig (*Annalen*, **241**, 161). We propose to publish our contribution to this large subject in a few short papers, like the present, each complete in itself.

*Oxyamidodisulphonates*, the subject of the present paper, are the *sulphazidates* of Fremy, the *sulphydroxylamates* of Claus, the *hydroxylamine-monosulphonates* of Raschig. Between the one set of terms—*nitrilo-*, *imido-*, and *amido-* *oximido-* and *oxyamido-sulphonates*—and the other set—*amine-* and *hydroxylamine-* *tri-*, *di-*, and *mono-sulphonates*—there is not much to choose. As, however, it is desirable, on the score of consistency, to employ exclusively either one set or the other, the use already prevalent of *nitrilo-*, *imido-*, and *amido-sulphonate* makes it advisable to employ the term *oximido-* and *oxyamido-sulphonate* rather than *hydroxylamine-* *di-* and *mono-sulphonate*.

*Oxyamidodisulphonic acid*, known only in solution, was first prepared by Fremy, who found that potassium oximidodisulphonate (neutral sulphazotate) sooner or later decomposed into acid sulphate and the oxyamido salt, the change taking place at once when the solution was boiled. Altering the atomic weights to those now accepted, and writing empirically his formulæ, to which he attached no constitutional significance, his equation becomes—



Claus has shown, however, that these formulæ do not correctly represent the composition of the salts; and Raschig has confirmed Claus's statement. The two formulæ corrected stand as  $\text{S}_4\text{O}_{15}\text{K}_4\text{H}_{10}\text{N}_2$  and  $\text{S}_2\text{O}_5\text{K}_2\text{H}_4\text{N}_2$ , or  $\text{HON}(\text{SO}_3\text{K})_2(\text{OH})_2$  and  $\text{HONH}(\text{SO}_3\text{K})$ , according to Claus. The latter formula we find it necessary to modify slightly.

To get the oxyamidodisulphonic acid pure for the preparation of its salts, Fremy neutralised the hydrolysed solution of potassium oximidodisulphonate with ammonia, added barium chloride, filtered off the sulphate, and then, by the addition of baryta-water, threw down a precipitate of a dibarium oxyamidodisulphonate. This salt when washed was decomposed by adding just enough sulphuric acid to combine with the barium; the filtered solution of the new acid being used for preparing the salts by combining it with the corresponding bases. The acid appears to be the only sulphoxyazotised acid pos-

\* He recognised the peculiarity and importance of this first instance of what we now style the hydrolysis of a sulphonate into a sulphate.

sessing any stability. Claus introduced a slight modification in Fremy's process by omitting the preliminary neutralisation with ammonia.

As we have discovered a second barium salt, which is neutral and soluble, we treat the barium precipitate in a different way and thereby avoid the contamination of the salts with sulphite, as the latter is always present in Fremy's barium precipitate (see the section of this paper headed "*Decomposition of Oxyamidosulphonates by Alkaline Bases*," p. 765). The dibarium salt is, as found by Fremy, very alkaline to litmus, and we add to it only enough sulphuric acid to remove half the barium as sulphate, getting a neutral solution which contains only monobarium oxyamidosulphonate; from this the acid and its salts can be prepared by adding the equivalent quantity of sulphuric acid or a sulphate. In order to determine the quantity of sulphuric acid required, it is necessary to estimate the barium in a portion of the solution.

Raschig prepares an impure acid from Fremy's solution obtained by boiling potassium oximidosulphonate so as to hydrolyse it into potassium sulphate and oxyamidosulphonate. To do this he removes the potassium sulphate by alcohol, and then concentrates the solution of the acid to a syrupy consistence.

*Sodium oxyamidosulphonate*, as prepared by Fremy and by us, is a clear, gummy liquid, as viscous as molasses; this when exposed over sulphuric acid under diminished pressure, never solidified or showed any sign of crystallisation. It is neutral in reaction.

*Potassium oxyamidosulphonate*, prepared and analysed by Fremy, by Claus, and by us, when crystallised from its hot solution forms six-sided plates, as stated by Fremy, but the plates are more often square; by spontaneous evaporation of the cold solution, however, thick tables and bold prisms are obtained. Claus found the crystals to be anhydrous, and Fremy's analysis and formula agree with this observation. Fremy's analytical results cannot be relied on, however, and we have already had to give an instance of this in the present paper, and shall have to give others. We differ from Claus, inasmuch as we find that all the crystals of this salt effloresce slowly over sulphuric acid, and on analysis give results indicating the presence of 1 mol.  $\text{H}_2\text{O}$ . The solutions show a great tendency to supersaturate, and it often becomes very difficult to crystallise them. When thoroughly dry, the crystals can be kept for months without undergoing much change, but if moist they are unstable, hydrolysing, and becoming acid to litmus. The acidity developed is that of hydroxyammonium sulphate, hardly showing with methyl-orange. When heated, they suddenly intumesce below  $100^\circ$ , and are completely decomposed.

To determine the sulphur and nitrogen, we hydrolysed the salt by heating it in a sealed tube with hydrochloric acid at  $130^{\circ}$ , following Raschig's process, which, however, gives somewhat irregular results, as we afterwards found (see the analysis of the dibarium salt). The hydroxylamine thus produced was estimated by iodine after addition of potassium hydrogen carbonate. Water could not be removed by exposure over sulphuric acid, at the ordinary temperature and pressure, rapidly enough to be convenient for analytical purposes; this and other sulphazotised salts retaining, according to our experience, part of their water of crystallisation with great tenacity. Neither could the water be conveniently driven off in the oven, because of the decomposition of the salt at about  $95^{\circ}$ ; we made a fairly good estimation of it, however, by moderately heating the salt in a Sprengel-vacuum in a long, bulbed tube containing also sulphuric acid. The following is a table of our results:—

	$\text{HONH}(\text{SO}_3\text{K}), \text{OH}_2$	<i>a.</i>	<i>b.</i>	
Potassium.....	23.08	22.53*	23.45	—
Sulphur .....	7.58	7.34	7.69	7.56
Oxyamidogen, $\text{HONH}$ ...	18.94	17.96	19.76	17.50
Water .....	10.39	—	9.29	—

Sample *a* was in prisms, *b* in tabular crystals. We have given much consideration to Claus's results, apparently carefully obtained, but we are unable to offer any explanation of their difference from ours. We have prepared the salt in winter and in summer (when he found it difficult to work), by evaporation of cold solutions and by cooling hot solutions, and have always obtained crystals which slowly effloresced in the desiccator.

*Dibarium oxyamidodisulphonate*, prepared by Fremy and by us, is a crystalline, alkaline, nearly insoluble salt. It dissolves in hydrochloric acid, and then shows, by the odour evolved, the presence of sulphite as an impurity, varying from a trace only to a considerable quantity. The only analytical datum given by Fremy is that the salt is formed from one equivalent of acid and two equivalents of baryta. We have analysed it and found for it a composition agreeing with the formula given by Fremy less the  $\text{H}_2$  by which his formulæ generally exceed those now adopted.

In this analysis and that of the following salt, we slightly modified the method of hydrolysis so as to get uniform and higher numbers

\* Slight loss of potassium sulphate during cooling known to have occurred.

for the hydroxylamine. The modification consisted in heating for some time with hydrochloric acid at  $100^{\circ}$  before raising the temperature to  $130^{\circ}$ . We find that hydroxyammonium sulphate itself may be rapidly heated with acid to  $130^{\circ}$ , or even higher, without getting low results, from which it would appear that at the moment of its formation at  $130^{\circ}$  from its sulphonic-derivative, hydroxylamine is less stable than when already formed. The constitution of the dibarium salt is expressed by the formula  $\text{Ba} \left\langle \begin{smallmatrix} \text{N}(\text{OH}) \cdot \text{SO}^+ \\ \text{N}(\text{OH}) \cdot \text{SO}^+ \end{smallmatrix} \right\rangle \text{Ba}, \text{OH}_2$ .

	Calculated.	Found.
Barium .....	53.31	53.13
Sulphur.....	12.45	12.41
Oximidogen, HON .....	12.06	12.02

*Barium oxyamidodisulphonate*, prepared by us, in solution first, as already described in this paper (p. 762), by adding just enough sulphuric acid to the dibarium salt to remove half its barium. The neutral liquid thus obtained yields crystals of the salt on evaporation over sulphuric acid; it is very soluble, and forms small, hard, brilliant, square, tabular crystals intermixed with minute square prisms; the crystals contain water. When long kept, it decomposes. Heated nearly to  $100^{\circ}$ , it suddenly and violently decomposes into gases and barium sulphate.

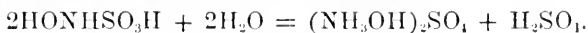
In analysing it, the barium was determined in one case by igniting it with sulphuric acid (*a*); in two cases the salt was slowly heated with dry sodium carbonate, whereby oxygen was absorbed from the air, after which the heat was raised until the mixture fused, and the barium and sulphur were then both determined (*b*); in another case the salt was hydrolysed by heating with hydrochloric acid, the separated barium sulphate (representing all the barium and half the sulphur of the salt) weighed, the other half of the sulphuric acid precipitated with barium chloride, and, lastly, the hydroxylamine titrated with iodine (*c*). The results were the following:—

	$(\text{HONHSO}_3)_2\text{Ba}, \text{OH}_2$	<i>a.</i>	<i>b.</i>		<i>c.</i>
Barium .....	36.15	36.17	36.27	35.88	35.53
Sulphur.....	16.88	—	16.84	16.65	16.49
Oxyamidogen, HONH .....	16.88	—	—	—	16.50

#### *The Hydrolysis of Oxyamidodisulphonic Acid.*

Although oxyamidodisulphonic acid is relatively stable, the fact that its solution does decompose was fully noticed by Fremy. Raschig

has found that the decomposition proceeds sharply, and, in presence of hot acid, rapidly, according to the equation—



With this important observation we fully agree from experience. Fremy stated that when the acid is boiled with water it decomposes wholly into acid ammonium sulphate, and oxygen or hydrogen peroxide. His finding ammonia and oxygen (or any gas) cannot be explained. He appears to have tested for hydrogen peroxide by adding manganese dioxide, which would account for his finding it, since an effervescence of nitrous oxide might easily pass for one of oxygen.

Claus expressed his hesitation to accept Fremy's equation (modified)— $2\text{HONH}(\text{SO}_3\text{H}) + 2\text{H}_2\text{O} = 2(\text{NH}_4)\text{HSO}_4 + \text{O}_2$ —as quantitative, but at the same time admitted that he had also obtained (besides sulphuric acid) ammonia and oxygen (or nitrous oxide). Raschig got other results, as already stated, and did not find either ammonia, or oxygen or nitrous oxide. These inexplicable differences have their parallel in what is contained in the next section of this paper, only there the differences noticed arise between ourselves and the other workers.

In presence of hydrogen potassium carbonate, oxyamidodisulphonates react with iodine solution like a hydroxylamine salt, only very much more slowly; so that their amount can be titrated in this way, without previous hydrolysis, though only with difficulty.

#### *Decomposition of Oxyamidodisulphonates by Alkaline Bases.*

The decomposition of oxyamidodisulphonates by a solution of potassium hydroxide appeared to have been fairly well worked out when we came to give attention to it. Fremy had observed that when heated with excess of this reagent the potassium salt disengaged ammonia as well as oxygen, of which, as he says, he had established the absolute purity by analysis. Hence it seemed that oxyamidodisulphonates undergo the same decomposition when heated with alkali as when heated with acid.

Lossen had just discovered hydroxylamine when work on the sulphazotised compounds was taken up by Claus, and this circumstance led the latter to see in the reaction between potassium hydroxide and Fremy's sulphazidate, as observed by Fremy and by himself, most convincing evidence that the salt is constituted as a sulphonic derivative of hydroxylamine, and is decomposed by the action of alkali into this base and potassium sulphate. He did not, he admits, succeed in isolating the hydroxylamine or any of its salts,

but he found all the sulphur of the sulphazidate converted into sulphate, and the other compounds in just the same proportions as Lossen had found when hydroxylamine is decomposed by heating with alkali, namely, ammonia equivalent to between a third and a half of the total nitrogen, and gases which neither extinguished nor rekindled a glowing match, and were, therefore, not the pure oxygen of Fremy's finding, but might well be nitrogen mixed with nitrous oxide as required on the supposition made. Added to this was the fact of the reducing action which the alkaline mixture exerted upon copper and silver salts, and the proof seemed complete.

Raschig, in his recent paper, went further in the matter than Claus, and, with or without experimental evidence—for we cannot decide from his words—concluded that an (unheated) alkaline solution of oxyamidosulphonic acid is actually a solution of free hydroxylamine, the latter being present in the quantity calculated from the amount of the acid taken, and, therefore, just such a solution of hydroxylamine as is wanted for preparing aldoximes and acetoximes.

Now, with two exceptions, namely, that nitrous oxide is given off, and that copper and silver salts are reduced—an action to be treated of in the following section of this paper—we are unable to confirm any of the observations of these chemists. This decomposition of oxyamidosulphonates by alkali is of another and still more interesting character than Claus and Raschig conceived it to be. That the oxyamidosulphonates are hydroxylamine-derivatives, which hydrolyse in *acid* solutions into hydroxylamine and sulphate, is, indeed, certain, as ascertained by Raschig. But, nevertheless, in *alkaline* solutions they give neither sulphate nor hydroxylamine, nor the decomposition-products of hydroxylamine.

Oxyamidosulphonates decompose with potassium hydroxide and similar reagents, exclusively into sulphite and hyponitrite, and the decomposition-products of a hyponitrite. No ammonia is formed, neither, so far as we could judge, any sulphate or any nitrogen, or, if any, only unimportant quantities of nitrogen and sulphate. The difficulty of keeping a sulphite solution for days free from sulphate, and of detecting small amounts of nitrogen in presence of nitrous oxide are well known and sufficiently explain any uncertainty in our results. The total absence of ammonia peremptorily forbids any admission of the generation of hydroxylamine.

Cold, dilute alkali, or alkaline-earth hydroxide suffices to partly effect the change under consideration. Consequently every attempt to form dipotassium or disodium oxyamidosulphonate corresponding with the dibarium salt has failed in our hands because of this resolution of the salt into simpler ones on the addition of alkali. For the same reason also, we find that Fremy's dibarium salt, described

in this paper, although insoluble, cannot be prepared quite free from sulphite, and when kept for any considerable time becomes charged with it, and also contains traces of hyponitrite.

To effect the complete or nearly complete conversion of these salts into sulphite and hyponitrite, they may be either left for days in the cold with the very strongest potassium hydroxide solution, or be heated to boiling for a short time with strong alkali. In both cases, effervescence occurs, due to the decomposition of hyponitrite. The gas evolved is not the feeble supporter of combustion met with by Claus, but behaves like oxygen, as Fremy had observed; it is not oxygen, however, but nitrous oxide, soluble in water. The highly alkaline liquid when acidified gives abundance of sulphur dioxide, and if neutralised merely will give, with barium chloride, a precipitate which might, of course, be taken for sulphate by a mind prepossessed, as Claus's almost admittedly was, and which does, as is well known, rapidly change into sulphate on the filter. When partially or fully neutralised with acetic acid, the solution, on treatment with sufficient silver nitrate, gives much silver hyponitrite, together with a very little reduced silver, owing to the sulphonic acid not being entirely destroyed. At first, the silver nitrate goes to form potassium silver sulphite, but this can be avoided if desired, either by using the barium salt instead of the potassium salt, or by adding barium hydroxide, and then filtering off the barium sulphite before adding the silver nitrite.

This decomposition actually furnishes by far the most productive method of preparing hyponitrite yet discovered. The following are the results of some trials we have made, the silver hyponitrite having been purified by the authors' method (*Trans.*, 1884, 45, 81), that is by dissolving it in nitric acid, and reprecipitating with sodium carbonate. Generally, the silver hyponitrite was directly weighed, but in one or two cases it was converted into chloride before weighing:—

Digestion of 0.5772 gram of crystals of potassium oxyamido-sulphonate for 24 hours with a saturated solution of potassium hydroxide containing some solid potash. It still contained a very small quantity of the sulphonic salt undecomposed, but the yield of hyponitrite in this case was 76 per cent. of the theoretical amount;

Boiling 0.9370 gram of crystals with concentrated potassium hydroxide for a short time was attended with copious effervescence of nitrous oxide, but still left a little of the salt undecomposed; the yield of hyponitrite, however, was 30 per cent. of the equivalent of the salt taken.

In order to prepare hyponitrite from nitrite in this way, there is no

necessity to have the oxyamidosulphonate pure; a well-prepared solution of either alkali salt sufficiently concentrated is all that is necessary if treated with solid potassium hydroxide. Working in this way, we found—

0.4545 gram of sodium nitrite\* after conversion into the sulphonic salt, and treatment in the cold with the most concentrated potash for 24 hours, gave hyponitrite amounting to 40 per cent. of the full yield, had all the nitrite been utilised;

0.5833 gram of sodium nitrate,\* after conversion, was treated first in the cold for 21 hours, and then at 100° for a quarter of an hour, and yielded hyponitrite amounting to  $49\frac{3}{4}$  per cent. of the calculated quantity.

In order to get results as good as these, however, one modification of the process for getting the oximidosulphonate from the nitrite must be followed; we reserve the account of this for the paper on these salts. Here we need only mention that we can get at least 85 per cent. of the calculated quantity of oximidosulphonate from the nitrite, a proportion far higher than that previously obtained by Raschig, the only quantitative worker.

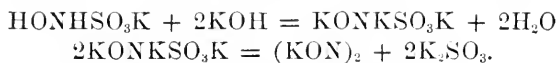
In consequence of the decomposition of much of the potassium hyponitrite into hydroxide and nitrous oxide, the determination of the hyponitrite found does not of itself serve to prove that the formation of this salt is the only decomposition of the oxyamidosulphonate. But it does make this deduction highly probable when taken along with the occurrence of so much nitrous oxide and sulphite, and the absence of ammonia, nitrogen, and sulphate. The determination of the sulphite, however, seems sufficient of itself to prove that the decomposition is of one kind only, although here, too, any very close approach to the calculated amount cannot be expected, considering the ready oxidisability of sulphites to sulphates, and that the sulphonate is never entirely decomposed. The presence of hyponitrite and its reaction with potassium iodide render a volumetric estimation of the sulphite by means of iodine impossible; in order, therefore, to estimate the sulphurous acid, we availed ourselves of its reaction with stannous chloride. The latter has no action either upon hydroxylamine (Divers and Haga, *Trans.*, 1885, **47**, 624), or upon oxyamidosulphonic acid. Our method of procedure was to put into a pressure-bottle the diluted solution of the salt decomposed by alkali and neutralised, mix it with excess of stannous chloride, and almost fill the bottle with water. The tightly closed bottle was kept in nearly boiling water for an hour, and then left to cool. The

\* Measured off for analysis as oxyamidosulphonate solution produced from a large quantity of nitrite worked upon.



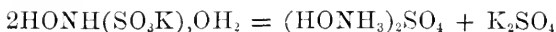
washed precipitate of stannous sulphide was heated with hydrochloric acid and potassium chlorate until all the sulphur had been oxidised, and the solution, after being evaporated to dryness, was again evaporated to dryness with hydrochloric acid. Finally, after removing the tin by hydrogen sulphide, the sulphuric acid in the filtrate was estimated as barium salt. In this way, from 0.7470 gram of salt, which by long keeping had slightly hydrolysed, we got sulphur equivalent to 88.63 per cent. of all that was in the original sulphonie salt. This result renders it clear that sulphite and, therefore, hyponitrite are the only two primary products of the change.

The reaction by which hyponitrite and sulphite are formed consists probably in the substitution of potassium for the hydrogen of the oxyamido-radicle, and then of spontaneous decomposition of the potassium compound. There is no hydrolysis or saponification, simply dissociation or chemical fission—



Raschig has observed a decomposition of Fremy's potassium sulphazite by strong potash into sulphite and nitrite very similar to this.

We would gladly account for the differences between the results found by other chemists and our own, but we are able to do little in this direction. We have to face the fact that Claus's work was quantitative. The only suggestion we can offer is that Fremy and Claus's preparations originally pure were not treated with alkali until they had been kept long enough to undergo the decomposition (fully in Claus's case)—



into hydroxylamine and sulphate. Such a mixture would behave exactly in the manner observed. As for oxygen, Fremy must have mistaken nitrous oxide for it, and in making this supposition we have evidently the support of Claus and Raschig. Lastly, as to Claus's nitrous oxide diluted with nitrogen, dilution with air and steam may perhaps have been the cause of the properties of the gas he got differing from that obtained by Fremy and ourselves.

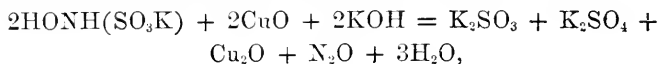
Oxyamidosulphonates evaporated to dryness on a water-bath with potassium or sodium carbonate evolve carbon dioxide during the last stages of the evaporation, and yield much sulphite. No hyponitrite can remain undecomposed under such circumstances. A solution of oxyamidosulphonate left even in the cold for a day with the carbonate shows evidence of the presence of a little sulphite.

After repeated evaporations with potassium acetate, an alkaline mixture containing a minute quantity of sulphite is left.

*Oxidation of Oxyamidosulphonates by Basic Reagents.*

Fremy observed that manganese dioxide dissolved as manganous salt in oxyamidosulphonic acid with effervescence due to evolution of oxygen, also that the same reagent caused a lively effervescence in a solution of the potassium salt. These observations are correct, save that he mistook nitrous oxide for oxygen. Finally, he found that the potassium salt immediately reduced salts of silver, copper, and gold. We must, however, except copper from this statement, unless alkali were present. Claus, as we have already had occasion to mention, found that the potassium salt, in the presence of potassium hydroxide, reduced salts of copper and silver in the cold, just like hydroxylamine; his experiments, however, were qualitative only. Raschig, who holds that alkalis convert oxyamidosulphonates wholly into their equivalent of hydroxylamine, records no experimental determinations in support of this point, though he quantitatively estimated the hydroxylamine produced by the action of an acid.

The reaction which we find takes place is the conversion of the oxyamidosulphonate into sulphite and sulphate, and the reduction of a quantity of metal-oxide equivalent to the oxidation of the oxyamido-residue, and not to that of the hydroxylamine supposed to be produced. That is to say, the cuprous oxide obtained is just half what it would be were hydroxylamine first formed, as believed by Claus and Raschig. The equation, therefore, will stand thus:—



which shows that the potassium hydroxide takes the two sulphonic residues to form sulphite, sulphate,\* and water, the copper oxide oxidising to water the two atoms of hydrogen of the two oxyamido-residues, the hyponitrous acid left being resolved finally into nitrous oxide and water. After the reduction, addition of hydrochloric acid liberates much sulphur dioxide.

The reaction is not quite complete, as it ceases when the solution becomes very dilute. Thus, if to an aqueous solution of 1 gram of the oxyamidosulphonate in a litre of water, a few drops only of a dilute solution of copper sulphate, and then of potassium hydroxide, are added, a permanent, blue opalescence is produced, but no cuprous oxide is deposited even when the solution is kept for hours in a

\* Hyposulphate was searched for, and could not be found.

closed vessel. This observation may serve to show that although, when very dilute, alkalis do not produce much sulphite and nitrite, this is not because hydroxylamine and sulphate are produced instead, for if such were the case, the hydroxylamine would act upon the cupric hydroxide.

The fact that the alkaline solution contains not hydroxylamine, but a sulphonie-derivative of it, which gives sulphite in its reactions with reducible compounds, and that it has only half the action of its equivalent of hydroxylamine, are serious, if not fatal, objections to resorting to it as a reagent in organic research for the purposes suggested by Raschig. This chemist, notwithstanding that he has pointed out (see his memoir, p. 182) that the reason that oximidosulphonates do not possess any of the reducing powers of hydroxylamine, is that in them the two active hydrogens of hydroxylamines are replaced by sulphonie radicles, and that oxyamidossulphonates by retaining one of these hydrogens are as easily oxidisable as hydroxylamine itself, has yet failed to see that, his contention being well-founded, it will be the oxyamidossulphonate, and not hydroxylamine, which exerts the reducing power in its alkaline solution. That it is so, is shown by the fact, determined by us, that in the absence of reducible agents, alkalis do not completely decompose oxyamidossulphonates, and for the rest change them into sulphite and hyponitrite, neither of which gives a cuprous precipitate in presence of alkalis.

We have yet to supply particulars of our quantitative work. It was unavoidable that the amount of sulphite produced should be imperfectly estimated, partly because of the great oxidisability of the very dilute alkaline sulphite by air, and partly because the decomposition of the oxyamidossulphonate is never complete. To measure it, the mother-liquor of the copper precipitate was run into excess of half-decinormal iodine solution (mixed with acid enough to more than neutralise the mother-liquor), and the unconsumed iodine titrated with sodium thiosulphate. The water used was always previously freed from air by boiling. Of the salt, 1.0967 grams treated with copper sulphate and potassium hydroxide gave in this way 40 per cent. of the sulphur of the salt as sulphite, and that was our best result. Theory, as given by us, indicates 50 per cent.; whilst on the other view there should be none at all. Other portions of the mother-liquor of the copper precipitate were acidified to promote the hydrolysis of any of the sulphonate remaining undecomposed, and afterwards concentrated by evaporation. One of these then gave a distinct reduction with the copper mixture, due to hydroxylamine; whilst another measured portion, on titration with iodine in presence of hydrogen potassium carbonate, also showed the presence of

hydroxylamine, equivalent, however, to only one-twelfth of the whole salt.

To measure the amount of copper reduced, we added to 0.2913 gram of the salt (already slightly hydrolysed by keeping) dissolved in water, a slight excess of a sort of Fehling's solution, much stronger than usual and with less alkali in it, heated to boiling, collected the cuprous oxide on a filter, washed rapidly, and weighed the reduced oxide as black oxide. We thus obtained cupric oxide equal to 48 per cent. of the weight of the salt, instead of 47 per cent., calculated from our equation. On the other theory, twice as much should have been obtained.

In alkaline solutions, silver and mercuric hydroxides act just like cupric hydroxide, qualitatively at least, and yield much sulphite.

*Constitution of Hyponitrites as revealed by the Decomposition of  
Oxyamidosulphonates.*

The decomposition of oxyamidosulphonates into sulphite and hyponitrite sets at rest any doubt as to the constitution of hyponitrites; for coming in this case directly from a substituted hydroxylamine, a hyponitrite must have its oxygen between the nitrogen and metal.

Berthelot and Maquenne have recently published papers (*Compt. rend.*, **108**, 1286, 1305) containing analyses of calcium and strontium hyponitrites. These analyses, as they point out, establish the accuracy of the empirical formula given by one of us (Divers) to hyponitrous acid, upon which doubt had been cast by previous work upon the silver salt by Berthelot himself and Ogier (*Compt. rend.*, **96**, 30, 84). To this salt the latter chemists gave the formula  $\text{Ag}_4\text{N}_4\text{O}_5$ , the correctness of which was afterwards contested by us (*Trans.*, 1884, **45**, 78). Berthelot now admits that this salt cannot be obtained in a pure state, thus confirming our view as against Zorn, van der Plaats and Menke, all of whom claimed to have got it in a pure state without difficulty. Zorn's opinion that the molecule of the acid contains 2 atoms of each of its elements, already generally accepted, is now endorsed by Berthelot and Maquenne. Lastly, Maquenne is disposed to deny that nitrous oxide can be the anhydride of hyponitrous acid, even to the same extent that carbon monoxide is the anhydride of formic acid, but on grounds which to us seem quite insufficient. Even the facts recorded in this paper can leave hardly any doubt that it is so.

The formula of hyponitrous acid may now confidently be written as  $\text{HO}\cdot\text{N}_2\cdot\text{OH}$ , or  $(\text{NOH})_2$ , that is, the acid is hydroximidogen, of which  $\text{NOH}$  is the radicle.





## APPENDIX.

We have again determined the sulphite produced both when potassium oxyamidodisulphonate is decomposed by potassium hydroxide alone, and also when it is oxidised by the same reagent and cupric oxide. In these determinations, the work was done in closed vessels excluding the air, so that no appreciable destruction of sulphite could have occurred through aerial oxidation. Also, in measuring the sulphite formed when the salt is oxidised by cupric oxide, we employed, here for the first time, the stannous chloride process described in the paper. The salt was treated with the cupric oxide in an atmosphere of hydrogen, in a bottle which was afterwards, without opening, filled up with stannous chloride and water. Only then and for a moment was the bottle opened, in order to remove the cork and gas tubes and insert the stopper before heating the mixture for an hour in boiling water. We feared that in washing the tin sulphides, the copper sulphides mixed with them would give trouble by oxidising on the filter, but our fears proved groundless.

For the other decomposition by alkali alone, we boiled the salt for a few hours with potassium hydroxide in a small tube in connection with a hydrogen-apparatus, and, when ready, quickly dropped this tube with its contents into the bottle of stannous chloride. With the precautions we have taken, we have now no longer to admit any imperfection known to us to have existed in our preparations for analysis, and can give the new results so far with confidence as being closely accurate.

The decomposition of the oxyamidodisulphonate by potassium hydroxide into hyponitrite and sulphite, using 0.2907 gram of freshly crystallised salt in fine plates, gave 89 per cent. (89.05) of the sulphur as sulphite, confirming our earlier result of 88 per cent. The oxidation of the salt by cupric oxide into sulphite, sulphate, and nitrous oxide, effected on 0.4298 gram of the above-described preparation, gave 44 per cent. (43.93) of the sulphur as sulphite, a result confirmatory of our theory, and better than our best previous result of 40 per cent.

It thus appears clear that the sulphite formed when the oxyamidodisulphonate is oxidised by cupric oxide is half what is produced when the salt is decomposed by alkali alone. That only nine-tenths of the reckoned sulphite is obtained in either case is partly if not entirely due to two causes. One of them is that, as already pointed out, in each mode of decomposition a little oxyamidodisulphonate (or a body like it) is always left at the end of the reaction. The other and main one is that the tin reaction is incomplete; for, working upon sulphite of a known degree of purity, we have got by its means only 91 and again  $93\frac{1}{2}$  per cent. of the sulphite indicated.





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## ERRATA.

## VOL. LV.

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16 20 from top, *for* “enumerate,” *read* “enunciate.”

17 last line, *after* "zinc," insert "in certain proportions."

18 2 from top, *omit* "brass."

18 3 „ *for “brass,” read “such a compound.”*

23 7 & 8        „        *for* “In fact, the water at this temperature is continually giving off fundamental molecules (that is, has a vapour-tension),” *read* “In the fact that water at this temperature is continually giving off fundamental molecules (that is, has a vapour-tension), we have a proof that.”

430 12 & 13 from top for " (m)NO<sub>3</sub>C<sub>6</sub>H<sub>4</sub>N<sub>3</sub>C<sub>10</sub>H<sub>6</sub>OH(β) . . . . . 52.74 "

$$(p) \text{Br} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH} (3) \dots\dots\dots 47.26''$$

read " (m)NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>N<sub>3</sub>C<sub>10</sub>H<sub>6</sub>OH(β) . . . . . 47.26"

(*p*) Br·C<sub>6</sub>H<sub>4</sub>·N<sub>2</sub>·C<sub>10</sub>H<sub>6</sub>·OH (*β*) . . . . . 52.74

761 5 „ for “25, 455,” read “25, 455 and 29, 422.”

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